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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

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Applicant: HESSELMANS, Laurentius, Cornelius, Josephus et al	

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- (71) Applicant (for all designated States except US): **STAHL INTERNATIONAL B.V.** [NL/NL]; Sluisweg 10, NL-5145 PE Waalwijk (NL).
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- (74) Agent: **KUPECZ, Arpad**; Octrooibureau Los en Stigter B.V., Weteringschans 96, NL-1017 XS Amsterdam (NL).
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(54) Title: PROCESS FOR THE PREPARATION OF A COATING, A COATED SUBSTRATE, AN ADHESIVE, A FILM OR SHEET, FOR THE THUS OBTAINED PRODUCTS AND THE COATING MIXTURE TO BE USED IN THE PROCESS

(57) Abstract: The invention comprises a process for the preparation of a coating, adhesive, film or sheet. In this process a mixture of a polyisocyanate functional, a polyepoxide functional, a polyanhydride functional or a polyketone functional compound or polymer and a compound containing reactive hydrogen, in which the compound containing reactive hydrogen is dispersed in a material which is non-reactive towards the compound containing reactive hydrogen, which mixture is not or low reactive at ambient conditions and high reactive under selected conditions, is applied onto a substrate at ambient temperature, followed by reacting the above compounds at elevated temperatures. At ambient temperature said compound containing reactive hydrogen is a solid material, a powder, a granule, a flake or grind or a mixture thereof which is preferably ground. The invention comprises further the coating mixtures to be used in the process and the coatings, coated substrates, adhesives, films, sheets, impregnated substrates, synthetic leathers, inmould coatings, coated leathers, coated polyvinylchlorides, coated non-wovens, coated coagulated polyurethane substrates, breathable coated substrates, obtained by applying the process.

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08G18/08 C08G18/10 C09J175/02				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08G C09J				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) WPI Data, EPO-Internal, PAJ				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 4 912 152 A (NEJIGAKI ET AL) 27 March 1990 (1990-03-27) column 1, line 43 -column 7, line 22; claims	1-7,11, 16,18,19		
X	EP 0 171 015 A (BAYER) 27 November 1985 (1985-11-27) page 1, line 1 -page 3, line 2 page 7, line 22 -page 21, line 16 page 47, line 24 -page 53, line 20	1,2		
X	US 4 552 913 A (WOLFE ET AL) 12 November 1985 (1985-11-12) column 1, line 59 -column 2, line 65; claims 1,2	1		
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.				
<input checked="" type="checkbox"/> Patent family members are listed in annex.				
* Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *8* document member of the same patent family </td> </tr> </table>			*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *8* document member of the same patent family
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *8* document member of the same patent family			
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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...orm in patent family members

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			AT 61607 T	15-03-1991
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			CA 2031224 A	07-06-1991
			JP 4100815 A	02-04-1992
			US 5077339 A	31-12-1991

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1013179 30 September 1999 (30.09.1999) **NL**
- (71) Applicant (for all designated States except US): **STAHL INTERNATIONAL B.V. [NL/NL]; Sluisweg 10, NL-5145 PE Waalwijk (NL).**
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **HESSELMANS, Laurentius, Cornelius, Josephus [NL/NL]; Vughterstraat 151/b, NL-5211 GB 's Hertogenbosch (NL). SPEK, Dirk, Pieter [NL/NL]; Hoog Meeuwen 19, NL-4268 GT Meeuwen (NL).**
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- (81) Designated States (national): **AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.**
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(54) Title: **PROCESS FOR THE PREPARATION OF A COATING, A COATED SUBSTRATE, AN ADHESIVE, A FILM OR SHEET, FOR THE THUS OBTAINED PRODUCTS AND THE COATING MIXTURE TO BE USED IN THE PROCESS**

(57) Abstract: The invention comprises a process for the preparation of a coating, adhesive, film or sheet. In this process a mixture of a polyisocyanate functional, a polyepoxide functional, a polyanhydride functional or a polyketone functional compound or polymer and a compound containing reactive hydrogen, in which the compound containing reactive hydrogen is dispersed in a material which is non-reactive towards the compound containing reactive hydrogen, which mixture is not or low reactive at ambient conditions and high reactive under selected conditions, is applied onto a substrate at ambient temperature, followed by reacting the above compounds at elevated temperatures. At ambient temperature said compound containing reactive hydrogen is a solid material, a powder, a granule, a flake or grind or a mixture thereof which is preferably ground. The invention comprises further the coating mixtures to be used in the process and the coatings, coated substrates, adhesives, films, sheets, impregnated substrates, synthetic leathers, inmould coatings, coated leathers, coated polyvinylchlorides, coated non-wovens, coated coagulated polyurethane substrates, breathable coated substrates, obtained by applying the process.

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Process for the preparation of a coating, a coated substrate, an adhesive, a film or sheet, for the thus obtained products and the coating mixture to be used in the process.

The present invention relates to a process to prepare a coating, adhesive, film or sheet, of the thus obtained products and to the coating mixture to be used in the process.

5 Several methods have been developed for high solids or solvent free application in the polyurethane industry to prepare coatings or films.

 One approach is the reaction of a polyisocyanate or of a isocyanate functional polyurethane prepolymer with
10 a polyol at 160-180°C. In this way flexible coatings can be prepared with a medium strength. A disadvantage of this method is that the potlife of the mixture is limited to about 3 hours.

 Further, while a reaction within 2 to 3 min is
15 required, there is only a partial reaction within that time and a post reaction takes place between the unreacted components during storage at ambient temperature. As a consequence the coatings are sometimes tacky immediately after the curing and for example a coated piece of textile
20 cannot be rolled up.

 A second approach is the reaction between a blocked polyisocyanate and a polyamine or polyol. Especially with polyamines strong films can be obtained. When the blocking agent is a ketoxime, such as butanone oxime,
25 it will evaporate during the reaction, but usually some of the butanone oxime will stay in the film. The result is that, also after application, there may be toxic vapours and the coating smells. Other types of blocking agents, such as dimethylpyrazole and triazole types, malonic esters or acetoacetates, and ϵ -caprolactams need a long de-
30 blocking time and they will partially stay in the coating as not-polymerized molecules. Also in these cases the coatings smell.

A further possibility is the combination of a polyisocyanate and a polyamine from which the amine functions are deactivated by the reaction with a maleic ester under formation of an aspartate. In spite of the deactivation of the amine functions the combination with a polyisocyanate will have a too limited potlife.

An alternative method is the use of internally blocked polyisocyanates which act as crosslinkers mainly in powder coatings. In this method an incorporated uretdion acts as internal blocking agent. At prolonged heating the uretdion unblocks under formation of two isocyanate functions, which further react with a material containing reactive hydrogen. The curing time at 180°C is at least 15 min, which is an unacceptable long time for our applications.

All these systems have some negative aspects such as a too short potlife, a too long reaction time and the evaporation of toxic vapours. We have overcome the described problems and have now developed a new process to prepare a coating, adhesive, film or sheet by a heat curable system.

Description of the invention

According to the present invention there is provided a process for the preparation of a coating, adhesive, film or sheet, characterized in that a mixture of a polyisocyanate functional, a polyepoxide functional, a polyanhydride functional or a polyketone functional compound or polymer and a compound containing reactive hydrogen, in which the compound containing reactive hydrogen is dispersed in a material which is non-reactive towards the compound containing reactive hydrogen, which mixture is not or low reactive at ambient conditions and high reactive under selected conditions, is applied onto a substrate at ambient temperature, followed by reacting the above compounds at elevated temperatures.

Surprisingly, the technical problems known in the art are solved and coatings, adhesives, films or sheet are obtained in an easy way by the process of the invention.

Surprisingly, it further appeared that the potlife of the coating mixtures of the invention is relatively long, the reaction is relatively fast and no toxic vapours are evaporated from the obtained products.

Since the material containing reactive hydrogen is not or low reactive at ambient temperature towards a polyisocyanate functional, a polyepoxide functional, a polyanhydride functional, or a poly ketone functional compound or polymer such mixtures will have a long pot-life, which is a great advantage in the process. This means, at ambient temperature, such a mixture will be stable for at least 1 day. Several of the compounds containing reactive hydrogen are that inert in a polyketone, polyepoxide or polyanhydride functional compound or polymer that the mixtures are stable as a one pot system.

The material containing reactive hydrogen, is not or low-reactive at ambient temperature because under these conditions the mixture of the isocyanate functional material and the material containing reactive hydrogen form a two phase system, which means it is a heterogeneous system. In the two phase system the compound containing reactive hydrogen is present in the mixture as a solid, a powder, a granule, a flake or a grind or a mixture thereof. The material is preferably ground to obtain a greater reactive area.

The compound containing reactive hydrogen is preferably dispersed in a second material, which material is non-reactive towards said compound containing reactive hydrogen, and not or low reactive towards the isocyanate functional-, the epoxide functional-, the anhydride functional- or the ketone functional compound or polymer at ambient temperature before the desired reaction is effected.

Such a dispersion is obtained by dispersing the material containing reactive hydrogen, in the second mate-

rial by conventional methods which may be by a for example a disperser or a pearl mill. By dispersing the compound containing reactive hydrogen in an inert material a smaller particle size and a greater area can be obtained than
5 when the pure solid is ground.

The compound containing reactive hydrogen reacts fast with a polyisocyanate functional, a polyepoxide functional, a polyanhydride, or a polyketone functional compound or polymer under selected conditions. Such a condition may be a sudden increase of temperature. At that moment the material containing reactive hydrogen will melt or dissolve in the system, the reactive sites of the molecules can move freely, and while the mixture is homogenised by diffusion, the reaction with the polyisocyanate
10 functional, the polyepoxide functional, the polyanhydride functional, or the polyketone functional compound or polymer occurs.

The homogenisation at higher temperatures will be more efficient and as a result the reaction will be faster and more complete. Moreover, the performance of the films or coatings will be better when the particle size of the material containing reactive hydrogen, is small.
20

An excellent film or coating quality is obtained when the particle size is between 0,5 and 200 μm . A more preferable particle size is between 0,5 and 60 μm and the most preferable size is between 0,5 and 15 μm .
25

To obtain a maximal potlife, the material containing reactive hydrogen may not melt or soften in the reaction mixture at ambient temperature.

Several types of material containing reactive hydrogen may be used in the process such as polyhydrazides, polysemicarbazides, polysulphonyl hydrazides, carbohydrazide, guanidine or guanidine salts, polyamines or polyamine salts.
30

Said polyhydrazide which may be used in the process of the invention may be oxalic dihydrazide, malonic dihydrazide, succinic dihydrazide, adipic dihydrazide, sebacic dihydrazide, dodecanoic dihydrazide, isophthalic di-
35

hydrazide, piperazine N,N'-dihydrazide, m-benzene-dihydrazide, p-benzene-dihydrazide.

Preferably adipic dihydrazide and carbodihydrazide are used since they are inert in the reaction mixtures with an epoxide functional-, an anhydride functional- or a ketone functional compound or polymer at ambient temperature for at least one year. They further reacts instantaneously with a polyisocyanate, a polyepoxide, a polyanhydride or a polyketone functional compound or polymer at temperatures of 80-180°C or higher.

A polysemicarbazide which may be used in the process of the invention is selected from ethane-disemicarbazide, butane-disemicarbazide, propane-disemicarbazide, hexane-disemicarbazide, para-benzene-disemicarbazide, toluene-2,4-disemicarbazide, toluene-2,4-disemicarbazide, bis (4-semicarbazido-phenyl)ether, bis (4,4'-hydrazido)-3,3'-dimethoxy biphenyl, di-N,N'-methylamino urea, 4,4'-methylene-bis(cyclohexene semicarbazide), 3-semicarbazido-methyl-3,5,5-trimethylcyclohexyl-semicarbazide or mixtures thereof.

A polysulphonylhydrazide which may be used in the process of the invention is selected from p,p'-oxybis benzene sulphonyl hydrazide; bis(methylhydrazido)sulphate, bis (methylhydrazidosulphonyl)piperazine, or bis p-(hydrazidosulphonylamino)benzene.

Usually, guanidine hydrochloride, guanidine acetate, guanidine carbonate and guanidine nitrate are suitable a guanidine salts.

A suitable polyamine or polyamine salt may be piperazine, piperazine diacetate, piperazine dihydrochloride, lysine, lysine hydrate, diaminoisophorone diacetate, diaminoisophorone dihydrochloride.

As mentioned before it is preferable when the compound containing reactive hydrogen is used as a dispersion in a material which is inert to both the reactive hydrogen compound and the second reagent of the reaction. This material is preferably a polyether, a polyester, a polycarbonate, a polyacrylate, a polyvinylalkylether, a

polyurethane, optionally substituted by substituents which are non reactive towards the material containing reactive hydrogen, and non- or low reactive towards the isocyanate functional material or is a plasticizer of the group of phthalic alkylesters, adipic alkyl esters, sebacic alkyl esters, dodecanoic alkyl esters, polyesters, phosphate esters, fatty esters, straight and modified natural or mineral oils, sulphonated oils, ethoxylated oils, epoxidised oils, fatty acids, sulphon amides, fat liquors, lecithine or a mixture thereof, optionally mixed with water.

An important aspect of the invention is that a low solvent level can be used during the process, and most preferably the process is solvent free.

In the process of the invention a polyisocyanate functional compound or polymer, a polyketone functional compound or polymer, a polyepoxide functional compound or polymer, or a polyanhydride functional compound or polymer and the material containing reactive hydrogen are mixed together in an stoichiometric ratio of 0.5 to 1.5, and preferably in a ratio of 0.9 to 1.2, whereafter the obtained mixture is applied onto a substrate and the covered or impregnated substrate is heated to a temperature of 50 to 300°C for 1-20 min and preferably to 80 to 200°C for 1 to 10 min.

Surprisingly it appeared that the reaction takes place as well when the polyisocyanate functional compound or polymer and the material containing reactive hydrogen are mixed together in a stoichiometric ratio of 0.5-1.5 and preferably in a ratio of 0.9 -1.1 whereafter the obtained mixture is applied onto a substrate and the covered or impregnated substrate is immersed into water of 20 to 100°C for 0.5 to 10 min.

The isocyanate functional compound or polymer which is used in the process of the invention is usually a polyisocyanate or a isocyanate functional polyurethane prepolymer.

Urea functions are formed by the reaction of the isocyanate functions and the NH_2 -functions of the material containing reactive hydrogen.

5 The ketone functional compound or polymer of the invention is preferably a ketone functional polymer polyurethane with in-chain, pendant and/or terminal ketone functions. Ketimine functions are formed by the reaction of the ketone and the NH_2 -functions of the material containing reactive hydrogen.

10 The anhydride functional compound of the invention is usually a polyanhydride or a copolymer containing anhydride functions. Amide functions are formed by the reaction of the anhydride function and the NH_2 -functions of the the material containing reactive hydrogen.

15 The epoxide functional compound of the invention is usually a polyepoxide or a epoxy functional polymer. The epoxide rings are opened during the reaction with the NH_2 -functions of the material containing reactive hydrogen and secondary or tertiary amines are formed.

20 A further part of the invention are the coatings, coated substrates, adhesives, films, sheets, impregnated substrates, synthetic leathers, inmould coatings, coated leathers, coated polyvinylchlorides, coated non-wovens, coated coagulated polyurethane substrates, breathable coated
25 substrates which are obtained by the process of the invention.

The thus obtained films or coatings are strong, dry, flexible and UV-resistant.

30 The process and application results of the present invention are profitable regarding to conventional heat curable systems which are low-solvent or solvent-free. Regarding to the system in which a polyisocyanate functional compound or polymer reacts with a polyol the mixture of the present invention has a longer pot life,
35 while the reaction is faster, almost instanteneous, and more complete at elevated temperatures. The obtained films or coatings are stronger because in the process of the invention urea functions are formed by the reaction of the

isocyanate function and the amine or hydrazide, while in the reaction of a isocyanate and a OH-function a urethane function is formed. It is wellknown that an urea function gives additional strength because of the presence of hydrogen at the N of the urea function which makes it possible to form hydrogen bridges.

Regarding to the systems in which blocked isocyanates are used in combination with polyamines films or coatings of comparable strength are formed by the process of the invention, but the elongation and the tension at break is larger. The potlife of the mixture of the present invention is longer, there are no evaporating toxic reactants such as butanone oxime, or remaining low molecular material such as dimethylpyrazole and triazole types, malonic esters or acetoacetates and the resulting films or coatings do not smell. As a consequence the process of the invention will not have any damaging effect on the environment.

Regarding to the systems in which a polyisocyanate is reacted with a polyamine from which the amine functions are deactivated by the reaction with a maleic ester under formation of a aspartate, the mixtures of the process of the invention have a much longer potlife.

Regarding to the system in which an incorporated uretdion acts as internal blocking agent the reaction time is much shorter at elevated temperatures.

Finally the invention provides a coating mixture comprising on the one side a isocyanatefunctional compound, a polyepoxide functional compound, a polyanhydride functional compound, or a polyketone functional compound and on the other side a compound containing a reactive hydrogen which is not or low reactive at ambient temperature and highly reactive under selected conditions, which coating mixture is applied in the process of the present invention.

The coating mixture of the invention is stable at ambient temperature for at least one day and preferably the coating mixture of the epoxide functional-, the anhy-

dride functional- or the ketone functional compound or polymer and the compound containing reactive hydrogen is stable at ambient temperature as a one pot system.

5 The compound containing reactive hydrogen is present in the mixture as a solid, a powder, a granule, a flake or a grind or a mixture thereof and is preferably ground.

10 As mentioned before it is preferable when the compound containing reactive hydrogen is used as a dispersion in a material which is inert to both the reactive hydrogen compound and the second reagent of the reaction.

15 The particle size of the ground or of the dispersion of the compound containing reactive hydrogen is from 0,5 to 200 μm , preferably from 0.5 to 60 μm and most preferably from 0.5 to 15 μm .

20 The mixtures of the isocyanate functional material and the material containing reactive hydrogen, may be applied onto a substrate. They may be used as films, sheets, in adhesives, sealants, printing ink and in coatings. They may be applied on any substrates, including leather or artificial leather, metals, wood, glass, plastics, paper, paper board, textile, non-woven, cloth, foam and the like by conventional methods, including spraying, flow-coating, reverse-coating, brushing, dipping, spreading and the like. The cured material may be further treated with coatings, such as a top-coat, or adhered to any substrate by direct or transfer coating technics.

25 Many additives may be present for application reasons, for example fillers, colorants, pigments, silicones, fire retardants, matting agents, flow agents, foaming agents and the like.

Some applications where the process of the invention is used are of special interest.

35 For example, the process may be used for the preparation of a coated textile to be used as a synthetic leather. Such a process may comprise the preparation of an adhesion coat onto textile, followed by applying a mixture of a polyurethane prepolymer and a hydrazide-, semicarba-

zide-, amine or amine salt- dispersion of the invention onto the adhesion coat and curing of this mixture at an elevated temperature, which may be between 80 and 250°C. The coating may further be embossed at 80 to 250°C.

5 By repeating of the process described above on the backside of the textile a double sided coated textile may be obtained.

Alternatively the process may be used for the preparation of a coated substrate to be used as synthetic leather by transfer coating, which may comprise the preparation of a skincoat onto release paper, followed by the preparation of an intermediate coat by applying a mixture of a polyurethane prepolymer and a hydrazide-, semicarbazide-, amine or amine salt- dispersion of the invention onto the skincoat and curing of this mixture at an elevated temperature, which may be between 80 and 250°C, whereafter an adhesive coat is applied onto the intermediate coat in which a piece of textile is laminated and the thus obtained material is dried, whereafter the release paper is removed.

The process described above may also be used for the preparation of for example coated leather, coated polyvinyl chloride, coated non-woven, coated coagulated polyurethane substrates.

25 Alternatively the process may be used for the preparation of a coated polyvinyl chloride to be used as synthetic leather by transfer coating, which may comprise the preparation of a skincoat onto release paper, followed by the preparation of an intermediate coat by applying a mixture of a polyurethane prepolymer and a hydrazide-, semicarbazide-, amine or amine salt- dispersion of the invention onto the skincoat and curing of this mixture at an elevated temperature, which may be between 80 and 250°C, whereafter a compact polyvinylchloride substrate onto the high solids coat is prepared by applying a polyvinylchloride paste onto the high-solids coat, optionally followed by laminating of a piece of textile into the polyvinyl-

chloride paste, and curing of the polyvinyl chloride paste.

The process may further be used in the preparation of a moulded material by inmould coating which comprises spraying of a mixture of a polyurethane prepolymer and a hydrazide-, semicarbazide-, amine or amine salt-dispersion of the invention, and optionally a non-reactive solvent into a matrix until a desired coating thickness is obtained. The matrix may be heated during the spray process, or after the spraying process. After the curing the moulded material may be removed.

Various aspects of the present invention are illustrated by the following examples. These examples are only illustrative of the invention and are not limiting the invention as claimed hereafter.

Examples

Example 1

Preparation of an aliphatic polyether based isocyanate functional polyurethane prepolymer.

Under a nitrogen atmosphere 112.78 g (507.56 mmole) of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate (hereafter referred to as IPDI) was added to a mixture of 139.21 g (138.24 mmole) of a polypropylene glycol with a molecular weight of 1007, 163.77 g (81.89 mmole) of a propylene glycol with a molecular weight of 2000 and 4.2 g (31.34 mmole) of trimethylol propane at 60-70°C while stirring. The mixture was heated to 100°C and reacted at this temperature for 2 hrs to form a polyurethane prepolymer. After 1 hr of reaction time 0.1 g of tinocctoate was added as a catalyst. The reaction mixture was cooled down. The amount of remaining NCO was measured and appeared to be 4.43%.

Example 2

Preparation of an aliphatic polyester based isocyanate functional polyurethane prepolymer.

Under a nitrogen atmosphere a 107.12 g (482 mmole) of IPDI was added to a mixture of 141.81 g (151.67 mmole) of a polyester diol with a molecular weight of 935 available from Occidental as Ruco S 1015-120, 166.83 g (55.61 mmole) of a polyesterdiol with a molecular weight of 3000 available from Occidental as Ruco S 1015-35 and 4.2 g (31.34 mmole) of trimethylol propane at 60-70°C while stirring. The mixture was heated to 100°C and reacted at this temperature for 2 hrs to form a polyurethane prepolymer. After 1 hr of reaction time 0.1 g of tinocatoate was added as a catalyst. The reaction mixture was cooled down. The amount of remaining NCO was measured and appeared to be 3.99%.

15 Example 3

Preparation of an aromatic polyether based isocyanate functional polyurethane prepolymer.

The procedure of example 1 was repeated with the exception that the IPDI was replaced by 88.31 g (507.56 mmole) of toluene diisocyanate (hereafter referred to as TDI) and the reaction was executed at 90-95°C. The NCO amount appeared to be 4.60%.

Example 4

25 Preparation of an aromatic polyester based isocyanate functional polyurethane prepolymer.

The procedure of example 2 was repeated with the exception that the IPDI was replaced by 85.61 g (492 mmole) of TDI and the reaction was executed at 90-95°C. The NCO amount appeared to be 4.23%.

Example 5

Preparation of a ketone functional polyurethane polymer from a isocyanate functional polyurethane prepolymer and hydroxyacetone

35 Under a nitrogen atmosphere a mixture of 100 g of the polyurethane prepolymer from example 1 and 7.81 g (105.48 mmole) of hydroxyacetone were heated to 100°C. The

mixture was stirred for 2 hrs at 100°C. After 1 hr of reaction time 0.1 g of tinocatoate was added as a catalyst. The disappearance of NCO was checked by IR-spectroscopy by following the NCO signal at 2269 cm⁻¹.

5

Example 6

Preparation of a ketone functional polyurethane polymer.

Under a nitrogen atmosphere 68.42 g (308 mmole) of IPDI was added to 251 g (171 mmole) of a ketone functional polyester diol obtainable from NeoResins as PEC 205 in 80 g of dipropylene glycole dimethyl ether at 60°C while stirring. The mixture was heated to 100°C and reacted at this temperature for 2 hrs to form a polyurethane prepolymer. After 1 hr of reaction time 0.1 g of tinocatoate was added as a catalyst. The reaction mixture was cooled down. The amount of remaining NCO was measured using a sample of 10 g, and appeared to be 2.71.

18.65 g (252 mmole) of methoxyethylamine was added to the obtained polyurethane prepolymer and the mixture was stirred for 15 min at 20°C. The disappearance of NCO was checked by IR-spectroscopy by following the NCO signal at 2269 cm⁻¹.

25

Example 7

Preparation of a ketone functional polyurethane polymer from a isocyanate functional isocyanurate and hydroxyacetone

Under a nitrogen atmosphere a mixture of 151 g (259 mmole) N,N',N''-triisocyanatohexylisocyanurate and 57.50 g (777 mmole) of hydroxyacetone in 52.13 g of dipropylene glycol dimethyl ether were heated to 90°C. The mixture was stirred for 2 hrs at 90°C. After 1 hr of reaction time 0.1 g of tinocatoate was added as a catalyst. The disappearance of NCO was checked by IR-spectroscopy by following the NCO signal at 2269 cm⁻¹.

35

Example 8

Comparative example: preparation of a film from a MEK-oxime blocked polyurethane polymer and a amine functional crosslinker.

5 9.39 g (105.48 mmole) of mekoxime was added to 100 g of the prepolymer of example 1 at 60-65°C. The mixture was stirred for 2 hrs at 70°C. The disappearance of the NCO was checked by the absence of the NCO-signal in the Infrared spectrum at 2270 cm⁻¹. The product was cooled
10 down and mixed with 12.47 g (52.4 mmole) of 3,3'-dimethyl-4,4'-diamino-dicyclohexyl-methan and 0.1 g of a 10 % solution of dibutyltinlaureate in dipropylene glycol dimethyl ether as catalyst.

200 µm films were prepared and cured at 180°C for
15 5 min.

Example 9

Comparative example: preparation of a film from a OH-functional polyurethane polymer and a NCO-crosslinker

20 A: preparation of the OH-functional polyurethane polymer:

Under a nitrogen atmosphere 264 g (132 mmole) of a polypropyleneglycol with a molecular weight of 2000 and 7.92 (88 mmole) of 1,3-butanediol were heated to 80°C.
25 97.68 (440 mmole) of IPDI was added and the mixture was stirred for 2 hrs at 100°C. After 1 hr of reaction time 0.1 g of tinocatoate was added as a catalyst. The reaction mixture was cooled down and the amount of remaining NCO in the resulting prepolymer was determined by titration and
30 appeared to be 4.6%. 36.21 g (402 mmole) of 1,3- butanediol and 0.1 g of dibutyl tinlaureate were added and the mixture was heated to 100° for two hrs. The disappearance of the NCO was checked by the absence of the NCO-signal in the Infrared spectrum at 2270 cm⁻¹. The product was cooled
35 down and had an OH-amount of 2.13 meq/g

B: preparation of an NCO-crosslinker: 14.4 g (240 mmole) of n-propanol was added within 30 min to 102.2 gr (containing 600 mmole of NCO) of N,N',N''-triisocyanato-

hexylisocyanurate, whereafter the mixture was stirred and heated at 80° for 2 hrs . After 1 hr of reaction time 0.1 g of tinocatoate was added as a catalyst. The reaction mixture was cooled down and the amount of remaining NCO in
5 the resulting polymer was determined by titration and appeared to be 12.0

A 200 μ m film was prepared from a mixture of 13 gr of the product of A and 9.2 g of the product of B with 0.05 g of a 10 % solution of dibutyltinlaureate in dipropylene glycol dimethyl ether as catalyst. The film was cured for 5 min at 160°C.
10

Example 10

Preparation of a semicarbazide from 4,4'-
15 methylene-bis(cyclohexylisocyanate) and hydrazine.

26.2 g (100 mmole) of 4,4'-ethylenebis(cyclohexylisocyanate) in 26.2 g of dipropylene glycol dimethyl ether was added to 12 g (240 mmole) of hydrazine hydrate in 18 g of isopropanol and 12 g of of dipropylene glycol dimethyl ether while keeping the temperature below 25°C by
20 cooling with ice. A white precipitate appeared. After stirring for 30 min the precipitate was filtered of and rinsed with dipropylene glycol dimethyl ether. The product was dried at 80°C. The yield was 44.42 g = 88.9 % from the
25 theoretical amount.

Example 11

Preparation of a semicarbazide from hexamethylene diisocyanate and hydrazine.

30 33.6 g (200 mmole) of hexamethylenediisocyanate in 33.6 g of dipropylene glycol dimethyl ether was added to 24 g (480 mmole) of hydrazinehydrate in 27 g of isopropanol and 24 g of of dipropylene glycol dimethyl ether while keeping the temperature below 25°C by cooling with
35 ice. A white precipitate appeared. After stirring for 30 min the precipitate was filtered of and rinsed with dipropylene glycol dimethyl ether. The product was dried at

80°C. The yield was 41.95 g = 84.9 % from the theoretical amount.

Example 12

5 Preparation of a semicarbazide from a commercial mixture of toluene diisocyanate and hydrazine.

34.8 g (200 mmole) of a commercial mixture of toluene diisocyanate in 33.6 g of dipropylene glycol dimethyl ether was added to 24 g (480 mmole) of hydrazine hydrate
10 in 24 g of isopropanol and 24 g of water while keeping the temperature below 25°C by cooling with ice. A white precipitate appeared. After stirring for 30 min the precipitate was filtered off and rinsed with dipropylene glycol dimethyl ether. The product was dried at 80°C.

15 The yield was 34.78 g = 69.3 % from the theoretical amount.

Example 13

20 Preparation of a semicarbazide from 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate and hydrazine.

44.4 g (200 mmole) of IPDI in 33.6 g of dipropylene glycol dimethyl ether was added to 24 g (480 mmole) of hydrazine hydrate in 24 g of isopropanol and 24 g of water while keeping the temperature below 25°C by cooling
25 with ice. The mixture was stirred for 1 hr and the solvents were evaporated. The mixture was crystallized from isopropanol.

Example 14

30 Preparation of a grind and of a dispersion of adipic dihydrazide.

Adipic dihydrazide was ground as a pure powder or it was ground in a 1:1 weight ratio in di(ethylhexyl) adipate in the presence of 0.5 % of Triton X-100. By increasing the dispersion time and the speed of the stirring
35 blade smaller particle sizes could be obtained. The grinds and dispersions which were obtained are presented in

Table I. The range of the particle size in the dispersions were measured by microscopy

5 **Table 1 Particle sizes of adipic dihydrazide in a pure grind or as a dispersion in di(ethylhexyl) adipate**

Example	medium	particle size of adipic dihydrazide in the medium (μm)
		Range
14 A	Pure	30-300
14 B	pure, ground	30-250
14 C	di(ethylhexyl)adipate	40-150
14 D	di(ethylhexyl)adipate	30- 60
14 E	di(ethylhexyl)adipate	5- 40
14 F	di(ethylhexyl)adipate	0.5-13

Example 15

10 Preparation of a dispersion of adipic hydrazide in different liquid materials which are none non-reactive towards the adipic dihydrazide.

Adipic hydrazide was dispersed in a 1:1 weight ratio in liquid materials which were non-reactive towards the adipic dihydrazide in the presence of 0.5 % of Triton X-100 by a Dispermat pearl mill configuration for 1.5 hrs at 5000 rpm. The range of the particle size in the dispersions depending on the medium were measured by microscopy. The results are presented in Table 2. The results show that the values for the particle size in a more polar medium are slightly less than in an apolar medium.

25 **Table 2 Particle size of adipic dihydrazide as dispersion in several media**

Example	medium	particle size of adipic dihydrazide in the medium (μm)
		range
15A	di(ethylhexyl)adipate	30 - 60
15B	dibutyl phthalate	30 - 60
15C	dioctyl phthalate	30 - 60
15D	dibutyl sebacate	30 - 60
15E	polyethylene glycol	10 - 30
15F	tributoxyethylphosphate	10 - 30
15G	soybean lecithin	10 - 30
15H	castor oil	10 - 30
15I	N-methyl pyrrolidone	10 - 30
15J	dipropylene glycol	10 - 30
	dimethylether	

Example 16

Preparation of a dispersion of several dihydrazides, disemicarbazides, a di(sulphonylhydrazide), amine salts.

Several dihydrazides, disemicarbazides, sulphonyldihydrazides and diamine salts were ground in di(ethylhexyl) adipate or in tributoxyethyl phosphate or in N-methylpyrrolidone by a Dispermat pearl mill configuration for 1.5 hrs at 5000 rpm. The products which were ground were: carbodihydrazide, oxalic dihydrazide, succinic dihydrazide, adipic dihydrazide, sebacic dihydrazide, dodecanoic dihydrazide, isophthalic dihydrazide, the products of example 10, 11, 12 and 13, 4,4'-oxybis(benzenesulphonylhydrazide), guanidine hydrochloride, lysine.

In all cases the particle sizes of the hydrogen reactive materials in the dispersions were measured by microscopy. The ranges in di(ethylhexyl) adipate were comparable and were between 30 and 60 μm . The values in tributoxyethyl phosphate or in N-methylpyrrolidone were slightly less and were 10-30 μm .

Example 17

Kinetics of the curing of the prepolymers of example 1, 2, 3 and 4 with adipic dihydrazide at several temperatures and times, measured by infrared spectroscopy.

The reaction of the prepolymers of example 1, 2, 3 and 4 with the adipic hydrazide dispersion of example 15 A (containing 5.716 meq of hydrazide/g) was followed at several temperatures by infrared spectroscopy. Further the potlife of the mixtures at 50°C were controlled.

50 gr of a polyurethane prepolymer of example 1, 2, 3, or 4 was mixed with a stoichiometric amount of the adipic dihydrazide dispersion and a film was prepared onto a sodium chloride cell. An Infrared spectrum was prepared which showed a large NCO signal at 2260 cm^{-1} . The cell was heated at 140, 160 or at 180°C for several minutes and the

decrease of the NCO-signal was measured by IR-spectroscopy. The results are presented in Table 3.

The results show that the IPDI-based prepolymers from example 1 and 2 are more reactive than the TDI-based prepolymers from example 3 and 4, which is indicated by a faster disappearance of the NCO-signal. There is not a significant difference in reactivity between the polyether and the polyester prepolymers.

Further the mixtures were stable for at least 6 weeks at 50°C and at that moment the intensity of the signals of the NCO in the IR-spectrum were comparable with that of the freshly prepared mixtures.

Table 3 decrease of the NCO signal in the infrared spectrum during the curing reaction of isocyanate functional prepolymers of example 1, 2, 3 and 4 with an adipic acid dispersion in di(ethylhexyl) adipate

Product of Example	Curing Temperature (°C)	amount of remaining NCO (%) after ^a			
		4 min	6 min	9 min	15 min
1	140	19.0	5.7	2.5	1.2
	160	1.5	0,3	0	0.3
2	140	26.5	5.9	2.2	1.2
	160	1.2	0.1	0	0
3	140	na	78.9	55.9	49.6
	160	na	25.2	10.3	8.2
	180	17.4	9	5.5	2.2
	200	3.2	1.5	1.0	0.7
4	140	na	89.0	58.8	51.1
	160	na	49.7	11.5	8.5
	180	19.4	9.8	5.6	2.4
	200	5.4	2.7	1.5	1.2

Notes to table 3:

a) determined by measuring the area of the signal at 2260-70 cm⁻¹ from the NCO-signal regarding to the carbonyl signal at 1740 cm⁻¹.

b) na = not available

Example 18

Kinetics of the film formation by curing of the polurethane prepolymer of example 2 and 4 with adipic dihydrazide or carbodihydrazide at several temperatures and times.

50 gr of polyurethane prepolymer of example 2 (based on IPDI, which is an alifatic diisocyanate) or 4 (based on TDI, which is an aromatic diisocyanate) were mixed with an stoichiometric amount of the adipic dihydrazide dispersion of example 15 A or of the carbodihydrazide dispersion of example 16 and the mixtures were applied on-to release paper. The curing of the films was checked at 120, 140 and at 160°C at 1, 2, 3, 6 and 12 min. The results are presented in tabel 4. Both, aromatic and aliphatic prepolymers are completely reacted with the carbodihydrazide or with the adipic dihydrazide after 3 min. at 160°C. Regarding to example 17 the reaction is faster because the sodium chloride cell needs more time for warming up than release paper. When the film formation was complete flexible films were obtained.

Table 4: Film formation by curing of a polyurethane prepolymer of example 2 and 4 with adipic dihydrazide or carbodihydrazide at several temperatures and times

poly-urethane of example	hydrogen reactive material	curing temp. (°C)	phase of the film ^{a)} at a curing time of				
			1 min	2 min	3 min	6 min	12 min
2	adipic dihydrazide	120	w	w	w	t	r
		140	t	r-i	r	r	r
		160	r-i	r	r	r	r
2	carbodi-hydrazide	120	w	w	t	t	r
		140	t	t	r-i	r	r
		160	r-i	r	r	r	r
4	adipic dihydrazide	140	w	w	w	w	t
		160	r-i	r	r	r	r
4	carbodi-hydrazide	140	r-i	r	r	r	r
		160	r-i	r	r	r	r

Notes to Table 4

a) w : the mixture is still wet; no reaction is observed

- t : the mixture is tacky; a partial reaction is effected
- r-i : film formation is effected, but the film is not strong, which means that the reaction is incomplete
- r : complete film formation is effected

Example 19

Preparation of films by curing a prepolymer of example 2 and adipic dihydrazide powder or dispersion of example 14 and measurement of the homogeneity of the films depending on the particle size of the adipic dihydrazide.

3.48 g (20 mmole) of ground adipic dihydrazide or 7.00 g (20 mmole) of an adipic dihydrazide dispersion in di(ethylhexyl)adipate of example 15 A was stirred into 50 g (containing 40 meq of NCO) of the prepolymer of example 2. Films of 200 μm were prepared onto a black coated glossy paper and heated for 3 min at 160°C. The gloss of the films was measured by a reflectometer. Further films of 200 μm were prepared on transparant polyester sheets and the transparency of the films was determined by measuring the transmission by spectroscopy at 550 nm on a Hitachi model 101 spectrophotometer. The gloss and the transparency of the films is a measure for the homogeneity of the films. The results of the tests are in table 5. It appeared that when the particle size of the adipic dihydrazide was small, the gloss and the transparency of the films were maximal.

Table 5: Homogeneity of cured films depending on the particle size of the adipic dihydrazide

Adipic hydrazide grind originated from example	particle size of the adipic dihydrazide in the grind (μm)	gloss of cured films of 200 μm	transmission of cured films of 200 μm (%)
	range		
14 A	30 - 300	7.8	52.2
14 B	30 - 250	8.5	64.5
14 C	40 - 150	27	85.0
14 D	30 - 60	46	93.5
14 E	5 - 40	60	94.6
14 F	0.5 - 13	95	97.0

Example 20

Preparation of a film by curing a polyether polyurethane prepolymer and an adipic dihydrazide dispersion and comparing the film with the film of example 8 and of example 9.

9.28 g (26.5 mmole) of an adipic dihydrazide dispersion of example 15 A was stirred into 50 g (containing 53 meq of NCO) of the prepolymer of example 1. Films of 200 μm were prepared and reacted for 3 min at 160°C. The mechanical properties of the films were determined and compared to those of the films of the high solid systems of comparative examples 8 and 9. The results are shown in table 6.

The results show that regarding to the films of example 8 and 9 the maximal strength and elongation of the film of example 20 is much higher. The tensile strength at 100 and 200 MPa is much more than that of example 9 and comparable with that of example 8. Regarding to example 8 there is a further advantage that no butanone oxime is released.

Table 6: mechanical properties of the films of a polyether polyurethane cured with adipic di-hydrazide regarding to the films of example 8 and of example 9.

Film of example	Mechanical properties (MPa) ^{a)}					
	M-100	M-200	M-300	M400	UTS	Elongation
8	2.6	3.8	-	-	4.7	260
9	0.6	1.2	-	-	1.3	220
20	2.8	4.4	5.8	7.7	7.8	405

notes to table 6:

a) MPa is megapascal (10^6 Nm^{-2}). The mechanical properties and the elongation are measured with films which were stretched at a thickness of 200 μm on a MTS Synergie 200 apparatus. The values at M-100, M-200, M-300 and M400 give tensile strengths of the films while stretching them for respectively 100, 200, 300 and 400 %. The UTS

is the ultimate tensile strength just before the film breaks. The elongation is the maximal elongation before the film breaks.

5 Example 21

Preparation of coatings on glass by curing a polyisocyanate and the adipic hydrazide dispersion of example 15A.

50 g of N,N',N''- tris(6-isocyanatohexyl)isocyanurate or of, N,N'-bis(6-isocyanato-hexyl-N-(6-isocyanato-hexylamido)urea was mixed with a stoichiometric amount of the adipic hydrazide dispersion of example 15A or of the carbodihydrazide dispersion of example 16. 200 μ m films were prepared on glass and heated for 6 min at 160°C. Hard coating surfaces were obtained with a good adhesion to the glass.

Example 22

Preparation of a film by curing a polyurethane prepolymer and a dispersion of a hydrogen reactive material of example 16.

50 g of the polyurethane prepolymer of example 2 was mixed with a stoichiometric amount of the dispersions of example 16 and the mixtures were applied onto release paper. The curing of the films was checked at 140 or 160°C after 3 min and after 12 min. When no film formation was observed the curing was checked at 220 and 250°C. The results are presented in tabel 7.

The results show that the dihydrazides, disemicarbazides and some diamine salts react with a isocyanate functional polyurethane prepolymer to form a film. These films are flexible. The table further shows that the reactivity of the used dihydrazides is comparable with that of the sulphonyldihydrazide used and both are more reactive than the semicarbazides used. The amine salts need a prolonged heating at higher temperatures before they react.

Table 7: Film formation by curing the polyurethane prepolymer of example 2 and a dihydrazide, disemicarbazide, and a diamine

Hydrogen reactive material	phase of the film ⁷⁷ at a curing temperature and time of						
	140°C		160°C		220°C		250°C
	3 min	12 min	3 min	12 min	3 min	12 min	3 min
carbodihydrazide	r-i	r	r	r	--	--	--
oxalic dihydrazide	t	r	r	r	--	--	--
succinic dihydrazide	t	r	r	r	--	--	--
adipic dihydrazide	r	r	r	r	--	--	--
sebacic dihydrazide	r	r	r	r	--	--	--
dodecanoic dihydrazide	r	r	r	r	--	--	--
isophthaltic dihydrazide	r	r	r	r	--	--	--
4,4'-methylenebis-(cyclohexylisemicarbazide)	w	w	w	t	r	--	--
hexamethylene disemicarbazide	w	w	t	r	r	--	--
tolyldisemicarbazide	w	w	w	t	r	--	--
3-semicarbazidomethyl-3,5,5-trimethylcyclohexylsemi-	w	w	w	r-i	r	--	--
carbazide 4,4'-oxybis-(benzenesulphonylhdyrazide)	r	r	r	r	--	--	--
guanidinehydrochloride	w	w	w	w	w	r	r-i
lysine	w	w	w	w	t	r	r-i

5

Notes to Table 7

a) w : the mixture is still wet; no reaction is observed

10 t : the mixture is tacky; a partial reaction is effected

r-i : film formation is effected, but the film is not strong, which means that the reaction is incomplete

r : complete film formation is effected

15

Example 23

Preparation of a film by curing a polyepoxide and a adipic dihydrazide or a carbodihydrazide dispersion

50 g (138.7 mmole) of Tetrad-X, which is a polyepoxide material obtainable from Mitsubishi, was mixed with a stoichiometric amount of the adipic hydrazide dispersion of example 15 A or the carbodihydrazide of example 16. The products were applied onto release paper and heated at 140 and at 160°C. The mixtures were cured after 6 min at 160°C or after 3 min at 180°C. Brittle films were obtained.

25

Example 24

Preparation of a film by curing a poly ketone functional compound and a adipic dihydrazide dispersion or a carbohydrazide dispersion.

5 The products of example 5, 6 and 7 and a mixture
20 % of example 7 + 80 % of example 5 were mixed with a
stoichiometric amount of the adipic dihydrazide dispersion
of example 15 A or with the carbodihydrazide dispersion of
example 16. The products were applied onto release paper.
10 The films were cured at 160°C during 3 min. The film for-
mation was complete. The films of the cured product of
examples 5 and 6 were very soft, sticky and flexible. The
film of the cured mixture was flexible and the film of the
cured product of example 7 was very hard.

15

Example 25

Preparation of a film by curing a polyanhydride
functional compound and a adipic dihydrazide dispersion.
20 gr of the styrene/anhydride copolymers, known as SMA
20 1000, SMA-2000 and SMA 3000 obtainable from Elf Atochem
were mixed with 8 g of 1-methoxy-propanol at 80°C until
the mixtures were dissolved. The solutions were cooled
down and mixed with a stoichiometric amount of the adipic
dihydrazide dispersion of example 15 A or with the carbo-
25 hydrazide dispersion of example 16 and applied onto glass
or onto release paper. The mixtures were cured at 160°C
for 6 min onto glass or for 4 min onto release paper. The
coatings obtained were extremely hard and brittle.

30

Example 26

Preparation of a coated textile to be used as
synthetic leather.

A coated textile was prepared by direct coating
comprising:

- 35 - Preparation of an adhesion coat onto textile: 150 μ m of
a mixture of 100 g RU-4049, 0.7 g of RM-4456, 5.0 g of
XR-5580 and 5 g water (products obtainable from

Stahl Holland) was applied onto textile by knife over roll and the coated textile was dried for 3 min at 80°C.

- Preparation of a coat from a solvent free material onto the thus obtained coated textile: 400 μ of a mixture of 100 g of the product of Example 1 and 21 g of the adipic hydrazide dispersion of example 15 A was applied onto the coated textile. The coating was cured in an oven at 160° for 3 min.
- The coating was embossed at 190°C.

10

Example 27

Preparation of a double sided coated textile which may be used as synthetic leather.

- 15 A double sided coated textile was prepared by direct coating by repeating the procedure of example 26 onto the other side of the textile.

Example 28

- 20 Preparation of a coated textile to be used as synthetic leather by transfer coating.

A coated textile was prepared by transfer coating comprising:

- Preparation of a topcoat onto release paper: 150 μ m of a 1:1 mixture of RU-3952 and RU3953 (both are aqueous polyurethane dispersions obtainable from Stahl Holland) containing 10 % of PP-3215 (a black pigment obtainable from Stahl Holland) was applied onto release paper by knife over roll and the coated paper was dried at 80°C for 3 min.
- 25 - Preparation of an intermediate coat from a solvent free material onto the coated release paper: 400 μ m of a mixture of 100 g of the product of Example 1 and 21 g of the adipic hydrazide dispersion of example 15 A was applied onto the topcoat. The coating on the paper was cured in an oven at 160° for 3 min.
- 30 - Preparation of an adhesive coat onto the obtained intermediate coat: 150 μ m of SU-6241 (which is a solvent based polyurethane obtainable from Stahl Holland) contain-
- 35

ning 5 % of XR-8041 (which is a crosslinker obtainable from Stahl Holland) was applied onto the intermediate coat.

- 5 - A piece of textile was laminated into the adhesive and the thus obtained material was dried at 120°C for 2 min.
- The release paper was removed from the thus coated textile.

Example 29

10 Preparation of a coated materials by transfer coating.

The procedure of example 28 was repeated with the exception that the textile was replaced by leather, non-woven or a coagulated polyurethane substrate.

15

Example 30

Preparation of a coated polyvinylchloride to be used as synthetic leather by transfer coating.

- 20 - Preparation of a skincoat onto release paper: 150 μ m of EX-51-550 (a solvent based polyurethane dispersions obtainable from Stahl Holland) was applied onto release paper by knife over roll and the coated paper was dried at 80°C for 3 min.
- 25 - Preparation of a coat from a high solids material onto the coated release paper: 400 μ m of a mixture of 100 g of the product of Example 2 and 17 g of the adipic hydrazide dispersion of example 15 A was applied onto the topcoat. The coating on the paper was cured in an oven at 160° for 3 min
- 30 - Preparation of a compact polyvinylchloride substrate onto the high solids coat: 400 μ m of a polyvinylchloride paste was applied onto the high-solids coat.
- a piece of textile was laminated in the polyvinyl chloride paste and the polyvinyl chloride was cured by 2 min
- 35 at 160°C followed by 1 min at 220°C.
- the release paper was removed from the thus coated polyvinylchloride on textile.

Example 31

Preparation of a moulded material by inmould coating.

A mixture of 100 g of example 2, 20 g of
5 N,N',N''- tris(6-isocyanatohexyl)isocyanurate and 37 g of
the adipic hydrazide dispersion of example 15 A was diluted
with 50 g of butylacetate and heated to 50°C while
mixing. The mixture was sprayed into a metallic matrix until
a coating of about 400 μm was obtained; the matrix was
10 pretreated with a silicon and was heated at 180°C during
the spray process. The matrix was cooled down and the
moulded material was removed.

CLAIMS

1. The process for the preparation of a coating, adhesive, film or sheet **characterized**, in that a mixture of a polyisocyanate functional, a polyepoxide functional, a polyanhydride functional or a polyketone functional compound or polymer and a compound containing reactive hydrogen, in which the compound containing reactive hydrogen is dispersed in a material which is non-reactive towards the compound containing reactive hydrogen, which mixture is not or low reactive at ambient conditions and high reactive under selected conditions, is applied onto a substrate at ambient temperature, followed by reacting the above compounds at elevated temperatures.

2. The process according to claim 1, **characterized**, in that at ambient temperature said compound containing reactive hydrogen is a solid material, a powder, a granule, a flake or grind or a mixture thereof which is preferably ground.

3. The process according to claims 1 and 2, **characterized**, in that the actual size of the grind of said compound containing reactive hydrogen, is from 0.5 to 200 μm and is preferably from 0.5 to 60 μm and is more preferably from 0,5 to 15 μm .

4. The process according to claims 1 to 3, **characterized**, in that said compound containing reactive hydrogen is a polyhydrazide, a polysemicarbazide, a polysulphonyl hydrazide, guanidine or a guanidine salt, a polyamine or blocked polyamine or is carbodihydrazide.

5. The process according to claim 4, **characterized**, in that said polyhydrazide is oxalic dihydrazide, malonic dihydrazide, succinic dihydrazide, adipic dihydrazide, sebacic dihydrazide, dodecanoic dihydrazide, isophthalic dihydrazide, piperazine N,N'-dihydrazide, m-benzene-dihydrazide, p-benzene-dihydrazide.

6. The process according to claims 4 or 5, **characterized**, in that the polyhydrazide is adipic dihydrazide or carbodihydrazide.

7. The process according to claim 4, **characterized**, in that said polysemicarbazide is ethane-disemicarbazide, butane-disemicarbazide, propane-disemicarbazide, hexane-disemicarbazide, para-benzene-disemicarbazide, toluene-2,4-disemicarbazide, toluene-2,4-disemicarbazide, bis (4-semicarbazido-phenyl)ether, bis (4,4'-hydrazido)-3,3'-dimethoxy biphenyl, di-N,N'-methylamino urea, 4,4'-methylene-bis(cyclohexene semicarbazide), 3-semicarbazido-methyl-3,5,5-trimethylcyclohexyl-semicarbazide or mixtures thereof.

8. The process according to claim 4, **characterized**, in that said polysulphonyl hydrazide is p,p'-oxybis benzene sulphonyl hydrazide; bis(methylhydrazido)sulphate, bis (methylhydrazidosulphonyl)piperazine, bis p-(hydrazidosulphonylamino)benzene.

9. The process according to claim 4, **characterized**, in that the guanidine salt is guanidine hydrochloride, guanidine acetate, guanidine carbonate, guanidine nitrate.

10. The process according to claim 4, **characterized**, in that the the polyamine or polyamine salt is piperazine, piperazine diacetate, piperazine dihydrochloride, lysine, lysine hydrate, diaminoisophorone diacetate, diaminoisophorone dihydrochloride.

11. The process according to claim 1, **characterized**, in that the material of claim 1 which is non-reactive towards said compound containing reactive hydrogen, is a polyether, a polyester, a polycarbonate, a polyacrylate, a polyvinylalkylether, a polyurethane, optionally substituted by substituents which are non reactive towards the material containing reactive hydrogen, and non- or low reactive towards the isocyanate functional material or is a plasticizer of the group of phthalic alkylesters, adipic alkyl esters, sebacic alkyl esters, dodecanoic alkyl esters, polyesters, phosphate esters, fatty esters, straight

and modified natural or mineral oils, sulphonated oils, ethoxylated oils, epoxidised oils, fatty acids, sulphon amides, fat liquors, lecithine or a mixture thereof, optionally mixed with water.

5 12. The process according to claims 1-11, **characterized**, in that the said mixture of the polyisocyanate functional, the polyepoxy functional, or the polyketone functional compound or polymer and the compound containing reactive hydrogen, is solvent free.

10 13. The process according to claims 1-12, **characterized**, in that said polyisocyanate functional compound or polymer and said compound containing reactive hydrogen are mixed together in a stoichiometric ratio of 0.5 to 1.5, and preferably in a ratio of 0.9 to 1,1, applied onto
15 a substrate and the so obtained covered or impregnated substrate is heated to a temperature of 50 to 300 °C for 1 to 20 min and preferably to a temperature of 80 to 200 °C for 1 to 10 min.

20 14. The process according to claims 1-12, **characterized**, in that said polyisocyanate functional compound or polymer and said compound containing reactive hydrogen are mixed together in a equivalent ratio of 0.5 to 1.5, and preferably in a ratio of 0,9 to 1,1, and applied onto a substrate whereafter the covered or impregnated substrate
25 is immersed into water of 20 to 100 °C for 1 to 10 min.

15. Coatings, coated substrates, adhesives, films, sheets, impregnated substrates, synthetic leathers, inmould coatings, coated leathers, coated polyvinylchlorides, coated non-wovens, coated coagulated polyurethane
30 substrates, breathable coated substrates, **characterised**, in that they are obtained by applying the process of any of the preceeding claims 1-14.

16. A coating mixture comprising a mixture of a polyisocyanate functional compound, a polyepoxide functional compound, a polyanhydride functional compound or a polyketone functional compound, and a compound containing reactive hydrogen which is not or low reactive at ambient
35 temperature and highly reactive under selected conditions,

which coating mixture is applied in the process of claim 1 to 15.

17. A coating mixture according to claims 1-16, **characterized**, in that the mixture of the polyisocyanate functional compound, the polyepoxide functional compound, the polyanhydride functional compound or the polyketone functional compound or polymers thereof and the compound containing reactive hydrogen is stable at ambient temperature for at least one day.

18. A coating mixture according to claims 16 or 17, **characterized**, in that the mixture of the polyepoxide functional compound, the polyanhydride functional compound or the polyketone functional compound or polymers thereof and the compound containing reactive hydrogen is stable at ambient temperature as a one pot system.

19. A coating mixture according to claims 16-18, **characterized**, in that the compound containing reactive hydrogen is present as grind which is dispersed in a material which is non-reactive towards the material containing reactive hydrogen.

20. A coating mixture according to claims 16-18, **characterized**, in that at ambient temperature the compound containing reactive hydrogen is a solid, which is a powder, a granule, a flake or a grind or a mixture thereof, which is preferably ground.

21. A coating mixture according to claims 16-18, **characterized**, in that the particle size of the ground or of the dispersion of the compound containing reactive hydrogen is from 0,5 to 200 μm , preferably from 0.5 to 60 μm and most preferably from 0.5 to 15 μm .

UP

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:	
OCTROOIBUREAU LOS EN STIGTER B.V.	
Attn. KUPEGZ, A.	
Weteringschans 96	
NL-1017 XS Amsterdam	WO 800 162
NETHERLANDS	
Ingek.	05 FEB. 2001
Termijn	06.4.2001 (06.03.2001)

Date of mailing (day/month/year)	06/02/2001
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Applicant's or agent's file reference WO 800162-KP	FOR FURTHER ACTION See paragraphs 1 and 4 below
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International application No. PCT/NL 00/00699	International filing date (day/month/year) 29/09/2000
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Applicant STAHL INTERNATIONAL B.V.

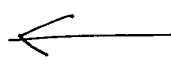
1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35



For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.


☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority  European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Alfredo Prein
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NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference WO 800162-KP	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/NL 00/ 00699	International filing date (day/month/year) 29/09/2000	(Earliest) Priority Date (day/month/year) 30/09/1999
Applicant STAHL INTERNATIONAL B.V.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

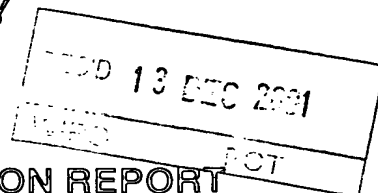
☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ **None of the figures.**

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)





Applicant's or agent's file reference WO 800162-Kp		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NL00/00699	International filing date (day/month/year) 29/09/2000	Priority date (day/month/year) 30/09/1999	
International Patent Classification (IPC) or national classification and IPC C08G18/08			
Applicant STAHL INTERNATIONAL B.V.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 8 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 13 sheets.

3. This report contains indications relating to the following items:
 - I ☒ Basis of the report
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☒ Certain observations on the international application

Date of submission of the demand 22/01/2001	Date of completion of this report 11.12.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Müller, M Telephone No. +49 89 2399 8665 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NL00/00699

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1,3,7-13,15-28	as originally filed			
2,2a-2b,4-6,14	as received on	08/10/2001	with letter of	05/10/2001

Claims, No.:

1-19	as received on	08/10/2001	with letter of	05/10/2001
------	----------------	------------	----------------	------------

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NL00/00699

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

see separate sheet

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	6-8, 12
	No:	Claims	1-5, 9-11, 13-19
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-19
Industrial applicability (IA)	Yes:	Claims	1-19
	No:	Claims	

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

re item I

The following amendments are considered to go beyond the application as originally filed:

(A) In new claim 1, the particular components of a certain mixture have a specific reactivity whereas in the original claim, the entire mixture, i.e., not only the certain components, had a certain reactivity. This amendment thus is not supported on original claim 1.

(B) In new claim 1, the reactivity of certain components in the mixture is expressed towards certain further components, whereas in original claim 1, the reactivity was expressed in general terms not restricted to a reactivity towards other components. This amendment thus is not based on original claim 1.

(C) The reactivity at elevated temperature in original claim 1 has been replaced by a reactivity at 50 - 300°C. As a basis original claims 13 and 14 are given. However, these claims are entirely silent about reactivities and thus cannot form a basis for said amendment.

(D) In new claim 1, it is stated that after application onto the substrate, a reaction takes place. As a basis original claim 13 is given. In this claim, however, after application onto the substrate, heating but not necessarily reacting takes place. Original claim 13 thus cannot form a basis for this amendment.

(E) The reaction in new claim 1 takes place at a temperature of 50 to 300°C for 1 to 10 minutes. These conditions are, however, not present in original claim 13 either. More in particular, in this claim heating takes place either at 50 to 300°C for 1 to 20 minutes or at 80 to 200°C for 1 to 10 minutes. New claim 1 thus is not supported by original claim 13. For the same reason, the amendment on page 6, lines 23 - 24 and new claim 13 lacks proper basis.

(F) In original claim 1, it was stated that the reactive hydrogen compound was dispersed in a non-reactive material in the mixture. New claim 1, however, implies that the reactive hydrogen compound is dispersed in the non-reactive material prior to forming the mixture. This is not supported by original claim 1.

The above amendments cannot be taken into account when drafting the international preliminary examination report (Rule 70.2(C) PCT).

r item V

The present invention

The present invention refers to a process wherein a mixture is applied onto a substrate and reacted at elevated temperature to a coating, adhesive, film or sheet. The mixture comprises

- (A) a polyisocyanate functional, a polyepoxide functional, a polyanhydride functional or a polyketone functional compound,
- (B) a polyhydrazide, polysemicarbazide, polysulphonylhydrazide or carbodihydrazide which is dispersed in
- (C) a material which is non-reactive towards the compound containing reactive hydrogen, such as a plasticizer.

According to the original claims, component (B) is dispersed in component (C) in said mixture.

The present invention further refers to a coating mixture to be applied in the claimed process and to the products resulting from that process.

Cited references

Reference is made to the following documents:

- D1: EP-A-0 171 015 (BAYER) 27 November 1985 (1985-11-27)
- D2: US-A-4 912 152 (NEJIGAKI ET AL) 27 March 1990 (1990-03-27)
- D3: US-A-4 552 913 (WOLFE ET AL) 12 November 1985 (1985-11-12)

Novelty and inventive step (Articles 33(2) and (3) PCT)

D1 discloses a process for the preparation of coatings applying a mixture comprising

- (a) a polyisocyanate compound and
- (b) coated stabilized polyamine particles with a particle size of about 1 - 50 microns and optionally a dihydrazide, such as adipic acid dihydrazide as reactive hydrogen-containing component suspended, e.g., in
- (c) a plasticizer, such as dioctylphthalate (page 10, lines 21 - 23, page 14, line 1 through page 15, line 8, page 27, lines 22 - 25 and page 42, lines 5 - 14, Example 1).

The mixture used in the process of D1 thus comprises all components used in the claimed process. It can be cured at, e.g., 120°C for 5 - 15 minutes (page 50, line 23). The dihydrazide is suspended, together with the polyamine, in the plasticizer. The dihydrazide is, e.g., adipic dihydrazide which is an exemplified dihydrazide of the

claimed invention (see page 4, line 37 of the present application) and thus is solid and non-reactive towards the plasticizer.

The mixture has a long term stability at low temperatures and can be rapidly transformed into coatings by application of polar solvents or temperatures above 100°C (page 15, lines 4 - 8 and page 24, line 23 through page 25, line 2). The polyisocyanate is present in an amount such that the molar ratio between NCO groups and reactive hydrogen atoms is 0.8 - 1.25 (page 15, lines 20 - 23). No solvent is present in the mixture (Example 1).

D1 thus is novelty-destroying to the subject-matter of claims 1 - 6, 11 - 13 and 15 - 21.

D2 discloses the preparation of coatings or adhesives comprising the step of applying a curable composition to, e.g., a Teflon sheet (see column 1, lines 5 - 11 and column 10, lines 25 - 35, Examples). The composition comprises

- (a) at least one polyisocyanate compound,
- (b) a compound (B) selected from dihydrazides, such as adipic dihydrazide, and polyamines, such as melamine and optionally
- (c) a plasticizer (column 1, lines 41 - 61, column 4, lines 5 - 26, column 5, line 15 and column 6, line 26).

The mixture applied in the process of D2 thus comprises all the components of the mixture applied in the claimed process. It is cured at a temperature of, e.g., 120°C for less than 2 minutes (Examples). Due to the fact that these components are applied as a one pack composition (column 1, lines 43 - 44), compound (B) is dispersed in the plasticizer together with the polyisocyanate as claimed in original claim 1. The mixture of D2 consequently has a reactivity as claimed.

Compound (B) of D2 preferably is ground to a particle size of 50 microns or less (column 5, lines 54 - 60). The molar ratio between the isocyanate groups of the polyisocyanate compound and the reactive groups of compound (B) is 0.5 - 3 (column 5, lines 20 - 26). No solvent is used in the process of D2 (see Examples). Consequently, D2 is novelty-destroying to the subject-matter of claims 1 - 6, 12, 13 and 15 - 21.

D3 discloses a process for the preparation of in-mold coatings wherein a composition is applied which comprises

- (a) a prepolymer made from a polyol component and an excess of a polyisocyanate component, which prepolymer thus is a polyisocyanate, and
- (b) a salt of 4,4'-diphenyl methane dianiline (a polyamine) dispersed in
- (c) polytetramethylene adipate (column 1, lines 8 - 9 and 60 - 64 and column 2, lines 49 - 60).

The composition applied in this process is relatively inactive at temperatures below 100°C but is heat activatable at higher temperatures (column 2, lines 1 - 3). No solvent is present in the process.

The claimed process and coating differs from that disclosed in D3 in that in the claimed process, components different from a polyamine are used as reactive hydrogen compound. The claimed process and coating thus is novel over D3.

From the fact that polyamines were present in the original application as an example of reactive hydrogen compounds, it can be deduced that the problems of the present application are already solved by polyamines as disclosed in D3. The objective problem to be solved thus is the provision of an alternative reactive hydrogen compound. As, however, at least a polyhydrazide, which is now contained as reactive hydrogen compound in amended claim 1, is a well known alternative (see, e.g., D1 or D2), the selection of this compound cannot involve an inventive step. The present claims therefore lack inventive step over D3.

re item VIII

(A) It is not clear which reactivities are to be covered by the term "low reactive" in original claim 1. Similarly, it is not clear which reactivities are to be covered by the term "high reactive". Further, it is unclear, which conditions are to be covered by the term "selected conditions" in original claim 1. For all these reasons, claim 1 lacks clarity and thus does not meet the requirements of Article 6 PCT.

(B) In the same way as in the case of claim 1, the term "low reactive" in claim 11 lacks clarity.

(C) As set out above for original claim 1, the wordings "low reactive" and "highly reactive" as used in claim 16 lack clarity (Article 6 PCT).

(D) The wording "which may done be by a for example a" on page 4, amended lines 1 -

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NL00/00699

2 is linguistically unclear.

New page

A further possibility is the combination of a polyisocyanate and a polyamine from which the amine functions are deactivated by the reaction with a maleic ester under formation of an aspartate. In spite of the deactivation of the amine functions the combination with a polyisocyanate will have a too limited potlife.

An alternative method is the use of internally blocked polyisocyanates which act as crosslinkers mainly in powder coatings. In this method an incorporated uretdion acts as internal blocking agent. At prolonged heating the uretdion unblocks under formation of two isocyanate functions, which further react with a material containing reactive hydrogen. The curing time at 180°C is at least 15 min, which is an unacceptable long time for our applications.

All these systems have some negative aspects such as a too short potlife, a too long reaction time and the evaporation of toxic vapours. We have overcome the described problems and have now developed a new process to prepare a coating, adhesive, film or sheet by a heat curable system.

Description of the invention

~~According to the present invention there is provided a process for the preparation of a coating, adhesive, film or sheet, characterized in that a mixture of a polyisocyanate functional, a polyepoxide functional, a polyanhydride functional or a polyketone functional compound or polymer and a compound containing reactive hydrogen, in which the compound containing reactive hydrogen is dispersed in a material which is non-reactive towards the compound containing reactive hydrogen, which mixture is not or low reactive at ambient conditions and high reactive under selected conditions, is applied onto a substrate at ambient temperature, followed by reacting the above compounds at elevated temperatures.~~

15 According to the present invention there is
provided a process for the preparation of a coating,
adhesive, film or sheet characterized, in that a mixture
of a polyisocyanate functional, a polyepoxide functional,
a polyanhydride functional or a polyketone functional
20 compound or polymer and a dispersion of a compound
containing reactive hydrogen, in which the compound
containing reactive hydrogen is a polyhydrazide, a
polysemicarbazide, a polysulphonylhydrazide,
carbodihydrazide, in a material which contains no groups
25 which are reactive towards the compound containing
reactive hydrogen, in which mixture the reactivities of
the isocyanate, epoxide, anhydride or the ketone functions
towards the hydrazide, semicarbazide, sulphonylhydrazide
or carbodihydrazide is absent or low at ambient conditions
30 and the reactivities are high at temperatures of 50 to
300°C, is applied onto a substrate at ambient temperature,
followed by reacting the above compounds at 50 to 300°C
for 1 to 10 min or is applied onto a substrate at ambient

temperature, followed by immersing the coated substrate into water of 20 to 100°C for 1 to 10 min.

✓done
rial by conventional methods which may be by a for example
a disperser or a pearl mill. By dispersing the compound
containing reactive hydrogen in an inert material a smaller
particle size and a greater area can be obtained than
5 when the pure solid is ground.

The compound containing reactive hydrogen reacts
fast with a polyisocyanate functional, a polyepoxide functional,
a polyanhydride, or a polyketone functional compound or polymer
under selected conditions. Such a condition may be a sudden
10 increase of temperature. At that moment the material containing
reactive hydrogen will melt or dissolve in the system, the reactive
sites of the molecules can move freely, and while the mixture is
homogenised by diffusion, the reaction with the polyisocyanate
15 functional, the polyepoxide functional, the polyanhydride functional,
or the polyketone functional compound or polymer occurs.

The homogenisation at higher temperatures will be more
efficient and as a result the reaction will be faster
20 and more complete. Moreover, the performance of the films or
coatings will be better when the particle size of the material
containing reactive hydrogen, is small.

An excellent film or coating quality is obtained when the
particle size is between 0,5 and 200 μm . A more
25 preferable particle size is between 0,5 and 60 μm and the most
preferable size is between 0,5 and 15 μm .

To obtain a maximal potlife, the material containing
reactive hydrogen may not melt or soften in the reaction
mixture at ambient temperature.

30 Several types of material containing reactive hydrogen may be
used in the process such as polyhydrazides, polysemicarbazides,
polysulphonyl hydrazides, carbonylhydrazide, ~~guanidine or guanidine salts, polyamines or polyamides~~
* ~~or ureas~~

35 Said polyhydrazide which may be used in the process of the
invention may be oxalic dihydrazide, malonic dihydrazide,
succinic dihydrazide, adipic dihydrazide, sebacic dihydrazide,
dodecanoic dihydrazide, isophthalic di-

hydrazide, piperazine N,N'-dihydrazide, m-benzene-dihydrazide, p-benzene-dihydrazide.

Preferably adipic dihydrazide and carbodihydrazide are used since they are inert in the reaction mixtures with an epoxide functional-, an anhydride functional- or a ketone functional compound or polymer at ambient temperature for at least one year. They further reacts instantaneously with a polyisocyanate, a polyepoxide, a polyanhydride or a polyketone functional compound or polymer at temperatures of 80-180°C or higher.

A polysemicarbazide which may be used in the process of the invention is selected from ethane-disemicarbazide, butane-disemicarbazide, propane-disemicarbazide, hexane-disemicarbazide, para-benzene-disemicarbazide, toluene-2,4-disemicarbazide, toluene-2,4-disemicarbazide, bis (4-semicarbazido-phenyl)ether, bis (4,4'-hydrazido)-3,3'-dimethoxy biphenyl, di-N,N'-methylamino urea, 4,4'-methylene-bis(cyclohexene semicarbazide), 3-semicarbazido-methyl-3,5,5-trimethylcyclohexyl-semicarbazide or mixtures thereof.

A polysulphonylhydrazide which may be used in the process of the invention is selected from p,p'-oxybis benzene sulphonyl hydrazide; bis(methylhydrazido)sulphate, bis (methylhydrazidosulphonyl)piperazine, or bis p-(hydrazidosulphonylamino)benzene.

Usually, guanidine hydrochloride, guanidine acetate, guanidine carbonate and guanidine nitrate are suitable a guanidine salts.

~~A suitable polyamine or polyamine salt may be piperazine, piperazine diacetate, piperazine dihydrochloride, lysine, lysine hydrate, diaminoisophorene diacetate, diaminoisophorene dihydrochloride.~~

As mentioned before it is preferable when the compound containing reactive hydrogen is used as a dispersion in a material which is inert to both the reactive hydrogen compound and the second reagent of the reaction. This material is preferably a polyether, a polyester, a polycarbonate, a polyacrylate, a polyvinylalkylether, a

polyurethane, optionally substituted by substituents which are non reactive towards the material containing reactive hydrogen, and non- or low reactive towards the isocyanate functional material or is a plasticizer of the group of phthalic alkylesters, adipic alkyl esters, sebacic alkyl esters, dodecanoic alkyl esters, polyesters, phosphate esters, fatty esters, straight and modified natural or mineral oils, sulphonated oils, ethoxylated oils, epoxidised oils, fatty acids, sulphon amides, fat liquors, lecithine or a mixture thereof, optionally mixed with water.

An important aspect of the invention is that a low solvent level can be used during the process, and most preferably the process is solvent free.

In the process of the invention a polyisocyanate functional compound or polymer, a polyketone functional compound or polymer, a polyepoxide functional compound or polymer, or a polyanhydride functional compound or polymer and the material containing reactive hydrogen are mixed together in an ~~stoichiometric~~ ^{equivalent} ratio of 0.5 to 1.5, and preferably in a ratio of 0.9 to 1.2, whereafter the obtained mixture is applied onto a substrate and the covered or impregnated substrate is heated to a temperature of 50 to 300°C for 1-20 min and preferably to 80 to 200°C for 1 to 10 min.

Surprisingly it appeared that the reaction takes place as well when the polyisocyanate functional compound or polymer and the material containing reactive hydrogen are mixed together in a ~~stoichiometric~~ ^{equivalent} ratio of 0.5-1.5 and preferably in a ratio of 0.9 -1.1 whereafter the obtained mixture is applied onto a substrate and the covered or impregnated substrate is immersed into water of 20 to 100°C for 0.5 to 10 min.

The isocyanate functional compound or polymer which is used in the process of the invention is usually a polyisocyanate or a isocyanate functional polyurethane prepolymer.

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Example 8

Comparative example: preparation of a film from a MEK-oxime blocked polyurethane polymer and a amine functional crosslinker.

MEK-

5 9.39 g (105.48 mmole) of ~~mek~~oxime was added to 100 g of the prepolymer of example 1 at 60-65°C. The mixture was stirred for 2 hrs at 70°C. The disappearance of the NCO was checked by the absence of the NCO-signal in the Infrared spectrum at 2270 cm⁻¹. The product was cooled
10 down and mixed with 12.47 g (52.4 mmole) of 3,3'-dimethyl-4,4'-diamino-dicyclohexyl-methan and 0.1 g of a 10 % solution of dibutyltinlaureate in dipropylene glycol dimethyl ether as catalyst.

15 200 µm films were prepared and cured at 180°C for 5 min.

Example 9

Comparative example: preparation of a film from a OH-functional polyurethane polymer and a NCO-crosslinker

20 A: preparation of the OH-functional polyurethane polymer:

Under a nitrogen atmosphere 264 g (132 mmole) of a polypropyleneglycol with a molecular weight of 2000 and 7.92 g (88 mmole) of 1,3-butanediol were heated to 80°C.
25 97.68 g (440 mmole) of IPDI was added and the mixture was stirred for 2 hrs at 100°C. After 1 hr of reaction time 0.1 g of tinocatoate was added as a catalyst. The reaction mixture was cooled down and the amount of remaining NCO in the resulting prepolymer was determined by titration and
30 appeared to be 4.6%. 36.21 g (402 mmole) of 1,3- butanediol and 0.1 g of dibutyl tinlaureate were added and the mixture was heated to 100° for two hrs. The disappearance of the NCO was checked by the absence of the NCO-signal in the Infrared spectrum at 2270 cm⁻¹. The product was cooled
35 down and had an OH-amount of 2.13 meq/g

B: preparation of an NCO-crosslinker: 14.4 g (240 mmole) of n-propanol was added within 30 min to 102.2 gr (containing 600 mmole of NCO) of N,N',N''-triisocyanato-

Druckexemplar

New claims

08. 10. 2001

(45)

Claim 1:

1. The process for the preparation of a coating,
5 adhesive, film or sheet **characterized**, in that a mixture
of a polyisocyanate functional, a polyepoxide functional,
a polyanhydride functional or a polyketone functional
compound or polymer and a dispersion of a compound
containing reactive hydrogen , which compound is a
10 polyhydrazide, a polysemicarbazide, a
polysulphonylhydrazide, carbodihydrazide, in a material
which contains no groups which are reactive towards the
compound containing reactive hydrogen, in which mixture
the reactivities of the isocyanate, epoxide, anhydride or
15 the ketone functions towards the hydrazide, semicarbazide,
sulphonylhydrazide or carbodihydrazide is absent or low at
ambient conditions and the reactivities are high at
temperatures of 50 to 300 °C, is applied onto a substrate
at ambient temperature, followed by reacting the above
20 compounds at 50 to 300 °C for 1 to 10 min, or is applied
onto a substrate at ambient temperature, followed by
immersing the coated substrate into water of 20 to 100 °C
for 1 to 10 min.

25 Claim 11:

The process according to Claim 1, **characterized**
in that the material which contains no groups which are
reactive towards the compound containing reactive
hydrogen, is a
30 polyether, a polyester, a polycarbonate, a polyacrylate, a
polyvinylalkylether, a polyurethane, a polyacrylate, a
polyvinylalkylether, a polyurethane, optionally
substituted by substituents which are non reactive towards
the material containing reactive hydrogen, and non- or low

reactive towards the isocyanate functional material or is a plasticizer of the group of phthalic alkylesters, adipic alkyl esters, sebacic alkyl esters, dodecanoic alkyl esters, polyesters, phosphate esters, fatty esters, 5 straight and modified natural or mineral oils, sulphonated oils, ethoxylated oils, epoxidised oils, fatty acids, sulphon amides, fat liquors, lecithine or a mixture thereof, optionally mixed with water.

10 Claim 16:

A coating mixture to be applied in the process of claim 1 to 15 wherein the coating mixture comprises a mixture of a polyisocyanate functional, a polyepoxyde functional, a polyanhydride functional or a polyketone 15 functional compound and a dispersion of a compound containing reactive hydrogen, which compound is a polyhydrazide, a polysemicarbazide, a polysulphonylhydrazide, carbodihydrazide, in a material which contains no groups which are reactive towards the 20 compound containing reactive hydrogen, in which mixture the reactivities of the isocyanate, epoxide, anhydride or the ketone functions towards the hydrazide, semicarbazide sulphonylhydrazide or carbodihydrazide is absent or low at ambient conditions and the reactivities are high at 25 temperatures of 50 to 300 °C or when the mixture is immersed into water.

CLAIMS

nieuw claim!
→

1. The process for the preparation of a coating, adhesive, film or sheet characterized, in that a mixture of a polyisocyanate functional, a polyepoxide functional, a polyhydrazide functional or a polyketone functional compound or polymer and a compound containing reactive hydrogen, in which the compound containing reactive hydrogen is dispersed in a material which is non-reactive towards the compound containing reactive hydrogen, which mixture is not or low reactive at ambient conditions and high reactive under selected conditions, is applied onto a substrate at ambient temperature, followed by reacting the above compounds at elevated temperatures.

2. The process according to claim 1, characterized, in that at ambient temperature said compound containing reactive hydrogen is a solid material, a powder, a granule, a flake or grind or a mixture thereof which is preferably ground.

3. The process according to claims 1 and 2, characterized, in that the actual size of the grind of said compound containing reactive hydrogen, is from 0.5 to 200 μm and is preferably from 0.5 to 60 μm and is more preferably from 0.5 to 15 μm .

X
4. The process according to claims 1 to 3, characterized, in that said compound containing reactive hydrogen is a polyhydrazide, a polysemicarbazide, a polysulphonyl hydrazide, guanidine or a guanidine salt, a polyamine or blocked polyamine or is carbodihydrazide.

4 ---
X. The process according to claim X, characterized, in that said polyhydrazide is oxalic dihydrazide, malonic dihydrazide, succinic dihydrazide, adipic dihydrazide, sebacic dihydrazide, dodecanoic dihydrazide, isophthalic dihydrazide, piperazine N,N'-dihydrazide, m-benzene-dihydrazide, p-benzene-dihydrazide.

08-10-2001

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1 -- 4 ~~X~~ The process according to claims ~~X~~ or ~~X~~, characterized, in that the polyhydrazide is adipic dihydrazide or carbodihydrazide.

5-1-1 ~~X~~. The process according to claim ~~X~~, characterized, in that said polysemicarbazide is ethane-disemicarbazide, butane-disemicarbazide, propane-disemicarbazide, hexane-disemicarbazide, para-benzene-disemicarbazide, toluene-2,4-disemicarbazide, toluene-2,4-disemicarbazide, bis (4-semicarbazido-phenyl)ether, bis
10 (4,4'-hydrazido)-3,3'-dimethoxy biphenyl, di-N,N'-methylamino urea, 4,4'-methylene-bis(cyclohexene semicarbazide), 3-semicarbazido-methyl-3,5,5-trimethylcyclohexyl-semicarbazide or mixtures thereof.

7-1-1 ~~X~~. The process according to claim ~~X~~, characterized, in that said polysulphonyl hydrazide is p,p'-oxybis benzene sulphonyl hydrazide; bis(methylhydrazido)sulphate, bis(methylhydrazidosulphonyl)piperazine, bis p-(hydrazidosulphonylamino)benzene.

8-1-1 ~~X~~. The process according to claim ~~X~~, characterized, in that the guanidine salt is guanidine hydrochloride, guanidine acetate, guanidine carbonate, guanidine nitrate.

9-1-1 ~~X~~. The process according to claim ~~X~~, characterized, in that the polyamine or polyamine salt is piperazine, piperazine diacetate, piperazine dihydrochloride, lysine, lysine hydrate, diaminoisophorone diacetate, diaminoisophorone dihydrochloride.

9-1-1 ~~X~~. The process according to claim 1, characterized, in that the material of claim 1 which is ~~is non-reactive~~ ^V ~~towards~~ said compound containing reactive hydrogen, is a polyether, a polyester, a polycarbonate, a polyacrylate, a polyvinylalkylether, a polyurethane, optionally substituted by substituents which are non reactive towards the material containing reactive hydrogen, and non- or low reactive
35 towards the isocyanate functional material or is a plasticizer of the group of phthalic alkylesters, adipic alkyl esters, sebacic alkyl esters, dodecanoic alkyl esters, polyesters, phosphate esters, fatty esters, straight

contains no groups which are reactive towards

and modified natural or mineral oils, sulphonated oils, ethoxylated oils, epoxidised oils, fatty acids, sulphon amides, fat liquors, lecithine or a mixture thereof, optionally mixed with water.

10-- 5-9 ~~12~~. The process according to claims ~~1-11~~, characterized, in that the said mixture of the polyisocyanate functional, the polyepoxy functional, or the polyketone functional compound or polymer and the compound containing reactive hydrogen, is solvent free.

11-- 1-10 10 ~~13~~. The process according to claims ~~1-12~~, characterized, in that said polyisocyanate functional compound or polymer and said compound containing reactive hydrogen are mixed together in a ^Vstoichiometric ratio of 0.5 to 1.5, and preferably in a ratio of 0.9 to 1.1, applied onto
15 a substrate and the so obtained covered or impregnated substrate is heated to a temperature of 50 to 300 °C for 1 to ¹⁰20 min and preferably to a temperature of ~~20~~ ¹⁵⁰ to 200 °C for 1 to ~~20~~ min.

12-- 1-10 ~~14~~. The process according to claims 1-12, characterized, in that said polyisocyanate functional compound or polymer and said compound containing reactive hydrogen are mixed together in a ^Vequivalent ratio of 0.5 to 1.5, and preferably in a ratio of 0.9 to 1.1, and applied onto
20 a substrate whereafter the covered or impregnated substrate is immersed into water of 20 to 100 °C for 1 to 10 min.

13 ~~15~~. Coatings, coated substrates, adhesives, films, sheets, impregnated substrates, synthetic leathers, inmould coatings, coated leathers, coated polyvinylchlorides, coated non-wovens, coated coagulated polyurethane
30 substrates, breathable coated substrates, characterised, in that they are obtained by applying the process of any of the preceeding claims 1-~~14~~.

12 ~~16~~. A coating mixture comprising a mixture of a polyisocyanate functional compound, a polyepoxide functional
35 nal compound, a polyanhydride functional compound or a polyketone functional compound, and a compound containing reactive hydrogen which is not or low reactive at ambient temperature and highly reactive under selected conditions,

hieuw claim 16 → ^{is now} word claim 14

which coating mixture is applied in the process of claim 1
to ~~25~~.

13
15 -- 1-14 ~~20~~. A coating mixture according to claims ~~2-25~~,
characterized, in that the mixture of the polyisocyanate
5 functional compound, the polyepoxide functional compound,
the polyanhydride functional compound or the polyketone
functional compound or polymers thereof and the compound
containing reactive hydrogen is stable at ambient tempera-
ture for at least one day.

16 - 10
-- 15 ~~20~~. A coating mixture according to claims ~~26~~ or
~~20~~, characterized, in that the mixture of the polyepoxide
functional compound, the polyanhydride functional compound
or the polyketone functional compound or polymers thereof
and the compound containing reactive hydrogen is stable at
15 ambient temperature as a one pot system.

17 14-16 ~~20~~. A coating mixture according to claims ~~26-28~~,
characterized, in that the compound containing reactive
hydrogen is present as grind which is dispersed in a mate-
rial which is non-reactive towards the material containing
20 reactive hydrogen.

18 14-16 ~~20~~. A coating mixture according to claims 16-18,
characterized, in that at ambient temperature the compound
containing reactive hydrogen is a solid, which is a pow-
der, a granule, a flake or a grind or a mixture thereof,
25 which is preferably ground.

19 14-16 ~~20~~. A coating mixture according to claims ~~15-18~~,
characterized, in that the particle size of the ground or
of the dispersion of the compound containing reactive hy-
drogen is from 0,5 to 200 μm , preferably from 0.5 to 60 μm
30 and most preferably from 0.5 to 15 μm .

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

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PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year) 11.12.2001

Applicant's or agent's file reference
WO 800162-Kp

IMPORTANT NOTIFICATION

International application No.
PCT/NL00/00699

International filing date (day/month/year)
29/09/2000

Priority date (day/month/year)
30/09/1999

Applicant
STAHL INTERNATIONAL B.V.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference WO 800162-Kp		FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/NL00/00699	International filing date (day/month/year) 29/09/2000	Priority date (day/month/year) 30/09/1999	
International Patent Classification (IPC) or national classification and IPC C08G18/08			
Applicant STAHL INTERNATIONAL B.V.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 8 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 13 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 22/01/2001	Date of completion of this report 11.12.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Müller, M Telephone No. +49 89 2399 8665 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL00/00699

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1,3,7-13,15-28	as originally filed		
2,2a-2b,4-6,14	as received on	08/10/2001 with letter of	05/10/2001

Claims, No.:

1-19	as received on	08/10/2001 with letter of	05/10/2001
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2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

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5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

see separate sheet

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	6-8, 12
	No:	Claims	1-5, 9-11, 13-19
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-19
Industrial applicability (IA)	Yes:	Claims	1-19
	No:	Claims	

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

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re item I

The following amendments are considered to go beyond the application as originally filed:

(A) In new claim 1, the particular components of a certain mixture have a specific reactivity whereas in the original claim, the entire mixture, i.e., not only the certain components, had a certain reactivity. This amendment thus is not supported on original claim 1.

(B) In new claim 1, the reactivity of certain components in the mixture is expressed towards certain further components, whereas in original claim 1, the reactivity was expressed in general terms not restricted to a reactivity towards other components. This amendment thus is not based on original claim 1.

(C) The reactivity at elevated temperature in original claim 1 has been replaced by a reactivity at 50 - 300°C. As a basis original claims 13 and 14 are given. However, these claims are entirely silent about reactivities and thus cannot form a basis for said amendment.

(D) In new claim 1, it is stated that after application onto the substrate, a reaction takes place. As a basis original claim 13 is given. In this claim, however, after application onto the substrate, heating but not necessarily reacting takes place. Original claim 13 thus cannot form a basis for this amendment.

(E) The reaction in new claim 1 takes place at a temperature of 50 to 300°C for 1 to 10 minutes. These conditions are, however, not present in original claim 13 either. More in particular, in this claim heating takes place either at 50 to 300°C for 1 to 20 minutes or at 80 to 200°C for 1 to 10 minutes. New claim 1 thus is not supported by original claim 13. For the same reason, the amendment on page 6, lines 23 - 24 and new claim 13 lacks proper basis.

(F) In original claim 1, it was stated that the reactive hydrogen compound was dispersed in a non-reactive material in the mixture. New claim 1, however, implies that the reactive hydrogen compound is dispersed in the non-reactive material prior to forming the mixture. This is not supported by original claim 1.

The above amendments cannot be taken into account when drafting the international preliminary examination report (Rule 70.2(C) PCT).

r item V

The present invention

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The present invention refers to a process wherein a mixture is applied onto a substrate and reacted at elevated temperature to a coating, adhesive, film or sheet. The mixture comprises

(A) a polyisocyanate functional, a polyepoxide functional, a polyanhydride functional or a polyketone functional compound,

(B) a polyhydrazide, polysemicarbazide, polysulphonylhydrazide or carbodihydrazide which is dispersed in

(C) a material which is non-reactive towards the compound containing reactive hydrogen, such as a plasticizer.

According to the original claims, component (B) is dispersed in component (C) in said mixture.

The present invention further refers to a coating mixture to be applied in the claimed process and to the products resulting from that process.

Cited references

Reference is made to the following documents:

D1: EP-A-0 171 015 (BAYER) 27 November 1985 (1985-11-27)

D2: US-A-4 912 152 (NEJIGAKI ET AL) 27 March 1990 (1990-03-27)

D3: US-A-4 552 913 (WOLFE ET AL) 12 November 1985 (1985-11-12)

Novelty and inventive step (Articles 33(2) and (3) PCT)

D1 discloses a process for the preparation of coatings applying a mixture comprising

(a) a polyisocyanate compound and

(b) coated stabilized polyamine particles with a particle size of about 1 - 50 microns and optionally a dihydrazide, such as adipic acid dihydrazide as reactive hydrogen-containing component suspended, e.g., in

(c) a plasticizer, such as dioctylphthalate (page 10, lines 21 - 23, page 14, line 1 through page 15, line 8, page 27, lines 22 - 25 and page 42, lines 5 - 14, Example 1).

The mixture used in the process of D1 thus comprises all components used in the claimed process. It can be cured at, e.g., 120°C for 5 - 15 minutes (page 50, line 23).

The dihydrazide is suspended, together with the polyamine, in the plasticizer. The dihydrazide is, e.g., adipic dihydrazide which is an exemplified dihydrazide of the

claimed invention (see page 4, line 37 of the present application) and thus is solid and non-reactive towards the plasticizer.

The mixture has a long term stability at low temperatures and can be rapidly transformed into coatings by application of polar solvents or temperatures above 100°C (page 15, lines 4 - 8 and page 24, line 23 through page 25, line 2). The polyisocyanate is present in an amount such that the molar ratio between NCO groups and reactive hydrogen atoms is 0.8 - 1.25 (page 15, lines 20 - 23). No solvent is present in the mixture (Example 1).

D1 thus is novelty-destroying to the subject-matter of claims 1 - 6, 11 - 13 and 15 - 21.

D2 discloses the preparation of coatings or adhesives comprising the step of applying a curable composition to, e.g., a Teflon sheet (see column 1, lines 5 - 11 and column 10, lines 25 - 35, Examples). The composition comprises

- (a) at least one polyisocyanate compound,
- (b) a compound (B) selected from dihydrazides, such as adipic dihydrazide, and polyamines, such as melamine and optionally
- (c) a plasticizer (column 1, lines 41 - 61, column 4, lines 5 - 26, column 5, line 15 and column 6, line 26).

The mixture applied in the process of D2 thus comprises all the components of the mixture applied in the claimed process. It is cured at a temperature of, e.g., 120°C for less than 2 minutes (Examples). Due to the fact that these components are applied as a one pack composition (column 1, lines 43 - 44), compound (B) is dispersed in the plasticizer together with the polyisocyanate as claimed in original claim 1. The mixture of D2 consequently has a reactivity as claimed.

Compound (B) of D2 preferably is ground to a particle size of 50 microns or less (column 5, lines 54 - 60). The molar ratio between the isocyanate groups of the polyisocyanate compound and the reactive groups of compound (B) is 0.5 - 3 (column 5, lines 20 - 26). No solvent is used in the process of D2 (see Examples). Consequently, D2 is novelty-destroying to the subject-matter of claims 1 - 6, 12, 13 and 15 - 21.

D3 discloses a process for the preparation of in-mold coatings wherein a composition is applied which comprises

- (a) a prepolymer made from a polyol component and an excess of a polyisocyanate component, which prepolymer thus is a polyisocyanate, and
- (b) a salt of 4,4'-diphenyl methane dianiline (a polyamine) dispersed in
- (c) polytetramethylene adipate (column 1, lines 8 - 9 and 60 - 64 and column 2, lines 49 - 60).

The composition applied in this process is relatively inactive at temperatures below 100°C but is heat activatable at higher temperatures (column 2, lines 1 - 3). No solvent is present in the process.

The claimed process and coating differs from that disclosed in D3 in that in the claimed process, components different from a polyamine are used as reactive hydrogen compound. The claimed process and coating thus is novel over D3.

From the fact that polyamines were present in the original application as an example of reactive hydrogen compounds, it can be deduced that the problems of the present application are already solved by polyamines as disclosed in D3. The objective problem to be solved thus is the provision of an alternative reactive hydrogen compound. As, however, at least a polyhydrazide, which is now contained as reactive hydrogen compound in amended claim 1, is a well known alternative (see, e.g., D1 or D2), the selection of this compound cannot involve an inventive step. The present claims therefore lack inventive step over D3.

re item VIII

(A) It is not clear which reactivities are to be covered by the term "low reactive" in original claim 1. Similarly, it is not clear which reactivities are to be covered by the term "high reactive". Further, it is unclear, which conditions are to be covered by the term "selected conditions" in original claim 1. For all these reasons, claim 1 lacks clarity and thus does not meet the requirements of Article 6 PCT.

(B) In the same way as in the case of claim 1, the term "low reactive" in claim 11 lacks clarity.

(C) As set out above for original claim 1, the wordings "low reactive" and "highly reactive" as used in claim 16 lack clarity (Article 6 PCT).

(D) The wording "which may done be by a for example a" on page 4, amended lines 1 -

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2 is linguistically unclear.

New page

A further possibility is the combination of a polyisocyanate and a polyamine from which the amine functions are deactivated by the reaction with a maleic ester under formation of an aspartate. In spite of the deactivation of the amine functions the combination with a polyisocyanate will have a too limited potlife.

An alternative method is the use of internally blocked polyisocyanates which act as crosslinkers mainly in powder coatings. In this method an incorporated uretdion acts as internal blocking agent. At prolonged heating the uretdion unblocks under formation of two isocyanate functions, which further react with a material containing reactive hydrogen. The curing time at 180°C is at least 15 min, which is an unacceptable long time for our applications.

All these systems have some negative aspects such as a too short potlife, a too long reaction time and the evaporation of toxic vapours. We have overcome the described problems and have now developed a new process to prepare a coating, adhesive, film or sheet by a heat curable system.

Description of the invention

~~According to the present invention there is provided a process for the preparation of a coating, adhesive, film or sheet, characterized in that a mixture of a polyisocyanate functional, a polyepoxide functional, a polyanhydride functional or a polyketone functional compound or polymer and a compound containing reactive hydrogen, in which the compound containing reactive hydrogen is dispersed in a material which is non-reactive towards the compound containing reactive hydrogen, which mixture is not or low reactive at ambient conditions and high reactive under selected conditions, is applied onto a substrate at ambient temperature, followed by reacting the above compounds at elevated temperatures.~~

15 According to the present invention there is
provided a process for the preparation of a coating,
adhesive, film or sheet characterized, in that a mixture
of a polyisocyanate functional, a polyepoxide functional,
a polyanhydride functional or a polyketone functional
20 compound or polymer and a dispersion of a compound
containing reactive hydrogen, in which the compound
containing reactive hydrogen is a polyhydrazide, a
polysemicarbazide, a polysulphonylhydrazide,
carbodihydrazide, in a material which contains no groups
25 which are reactive towards the compound containing
reactive hydrogen, in which mixture the reactivities of
the isocyanate, epoxide, anhydride or the ketone functions
towards the hydrazide, semicarbazide, sulphonylhydrazide
or carbodihydrazide is absent or low at ambient conditions
30 and the reactivities are high at temperatures of 50 to
300°C, is applied onto a substrate at ambient temperature,
followed by reacting the above compounds at 50 to 300°C
for 1 to 10 min or is applied onto a substrate at ambient

temperature, followed by immersing the coated substrate into water of 20 to 100°C for 1 to 10 min.

4

✓ done

rial by conventional methods which may be by a for example
a disperser or a pearl mill. By dispersing the compound
containing reactive hydrogen in an inert material a smaller
particle size and a greater area can be obtained than
5 when the pure solid is ground.

The compound containing reactive hydrogen reacts
fast with a polyisocyanate functional, a polyepoxide functional,
a polyanhydride, or a polyketone functional compound or polymer
under selected conditions. Such a condition may be a sudden
10 increase of temperature. At that moment the material containing
reactive hydrogen will melt or dissolve in the system, the reactive
sites of the molecules can move freely, and while the mixture is
homogenised by diffusion, the reaction with the polyisocyanate
15 functional, the polyepoxide functional, the polyanhydride
functional, or the polyketone functional compound or polymer
occurs.

The homogenisation at higher temperatures will be
more efficient and as a result the reaction will be faster
20 and more complete. Moreover, the performance of the films
or coatings will be better when the particle size of the
material containing reactive hydrogen, is small.

An excellent film or coating quality is obtained
when the particle size is between 0,5 and 200 μm . A more
25 preferable particle size is between 0,5 and 60 μm and the
most preferable size is between 0,5 and 15 μm .

To obtain a maximal potlife, the material containing
reactive hydrogen may not melt or soften in the reaction
mixture at ambient temperature.

30 Several types of material containing reactive hydrogen
may be used in the process such as polyhydrazides,
polysemicarbazides, polysulphonyl hydrazides, carbohydra-
zide, ~~guanidine or guanidine salts, polyamines or polyami-~~
~~ne salts~~

35 Said polyhydrazide which may be used in the process
of the invention may be oxalic dihydrazide, malonic
dihydrazide, succinic dihydrazide, adipic dihydrazide, se-
bacic dihydrazide, dodecanoic dihydrazide, isophthalic di-

hydrazide, piperazine N,N'-dihydrazide, m-benzene-dihydrazide, p-benzene-dihydrazide.

Preferably adipic dihydrazide and carbodihydrazide are used since they are inert in the reaction mixtures with an epoxide functional-, an anhydride functional- or a ketone functional compound or polymer at ambient temperature for at least one year. They further reacts instantaneously with a polyisocyanate, a polyepoxide, a polyanhydride or a polyketone functional compound or polymer at temperatures of 80-180°C or higher.

A polysemicarbazide which may be used in the process of the invention is selected from ethane-disemicarbazide, butane-disemicarbazide, propane-disemicarbazide, hexane-disemicarbazide, para-benzene-disemicarbazide, toluene-2,4-disemicarbazide, toluene-2,4-disemicarbazide, bis (4-semicarbazido-phenyl)ether, bis (4,4'-hydrazido)-3,3'-dimethoxy biphenyl, di-N,N'-methyldiamino urea, 4,4'-methylene-bis(cyclohexene semicarbazide), 3-semicarbazido-methyl-3,5,5-trimethylcyclohexyl-semicarbazide or mixtures thereof.

A polysulphonylhydrazide which may be used in the process of the invention is selected from p,p'-oxybis benzene sulphonyl hydrazide; bis(methylhydrazido)sulphate, bis (methylhydrazidosulphonyl)piperazine, or bis p-(hydrazidosulphonylamino)benzene.

Usually, guanidine hydrochloride, guanidine acetate, guanidine carbonate and guanidine nitrate are suitable a guanidine salts.

* ~~A suitable polyamine or polyamine salt may be piperazine, piperazine diacetate, piperazine dihydrochloride, lysine, lysine hydrate, diaminoisophorone diacetate, diaminoisophorone dihydrochloride.~~

As mentioned before it is preferable when the compound containing reactive hydrogen is used as a dispersion in a material which is inert to both the reactive hydrogen compound and the second reagent of the reaction. This material is preferably a polyether, a polyester, a polycarbonate, a polyacrylate, a polyvinylalkylether, a

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polyurethane, optionally substituted by substituents which are non reactive towards the material containing reactive hydrogen, and non- or low reactive towards the isocyanate functional material or is a plasticizer of the group of phthalic alkylesters, adipic alkyl esters, sebacic alkyl esters, dodecanoic alkyl esters, polyesters, phosphate esters, fatty esters, straight and modified natural or mineral oils, sulphonated oils, ethoxylated oils, epoxidised oils, fatty acids, sulphon amides, fat liquors, lecithine or a mixture thereof, optionally mixed with water.

An important aspect of the invention is that a low solvent level can be used during the process, and most preferably the process is solvent free.

In the process of the invention a polyisocyanate functional compound or polymer, a polyketone functional compound or polymer, a polyepoxide functional compound or polymer, or a polyanhydride functional compound or polymer and the material containing reactive hydrogen are mixed together in an ~~stoichiometric~~ ^{equivalent} ratio of 0.5 to 1.5, and preferably in a ratio of 0.9 to 1.2, whereafter the obtained mixture is applied onto a substrate and the covered or impregnated substrate is heated to a temperature of 50 to 300°C for 1-20 min and preferably to 80 to 200°C for 1 to 10 min.

Surprisingly it appeared that the reaction takes place as well when the polyisocyanate functional compound or polymer and the material containing reactive hydrogen are mixed together in a ~~stoichiometric~~ ^{equivalent} ratio of 0.5-1.5 and preferably in a ratio of 0.9 -1.1 whereafter the obtained mixture is applied onto a substrate and the covered or impregnated substrate is immersed into water of 20 to 100°C for 0.5 to 10 min.

The isocyanate functional compound or polymer which is used in the process of the invention is usually a polyisocyanate or a isocyanate functional polyurethane prepolymer.

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Example 8

Comparative example: preparation of a film from a MEK-oxime blocked polyurethane polymer and a amine functional crosslinker.

MEK-

5 9.39 g (105.48 mmole) of ~~max~~oxime was added to 100 g of the prepolymer of example 1 at 60-65°C. The mixture was stirred for 2 hrs at 70°C. The disappearance of the NCO was checked by the absence of the NCO-signal in the Infrared spectrum at 2270 cm⁻¹. The product was cooled
10 down and mixed with 12.47 g (52.4 mmole) of 3,3'-dimethyl-4,4'-diamino-dicyclohexyl-methan and 0.1 g of a 10 % solution of dibutyltinlaureate in dipropylene glycol dimethyl ether as catalyst.

15 200 µm films were prepared and cured at 180°C for 5 min.

Example 9

Comparative example: preparation of a film from a OH-functional polyurethane polymer and a NCO-crosslinker

20 A: preparation of the OH-functional polyurethane polymer:

Under a nitrogen atmosphere 264 g (132 mmole) of a polypropyleneglycol with a molecular weight of 2000 and 7.92 (88 mmole) of 1,3-butanediol were heated to 80°C.
25 97.68 (440 mmole) of IPDI was added and the mixture was stirred for 2 hrs at 100°C. After 1 hr of reaction time 0.1 g of tinocatoate was added as a catalyst. The reaction mixture was cooled down and the amount of remaining NCO in the resulting prepolymer was determined by titration and
30 appeared to be 4.6%. 36.21 g (402 mmole) of 1,3- butanediol and 0.1 g of dibutyl tinlaureate were added and the mixture was heated to 100° for two hrs. The disappearance of the NCO was checked by the absence of the NCO-signal in the Infrared spectrum at 2270 cm⁻¹. The product was cooled
35 down and had an OH-amount of 2.13 meq/g

B: preparation of an NCO-crosslinker: 14.4 g (240 mmole) of n-propanol was added within 30 min to 102.2 gr (containing 600 mmole of NCO) of N,N',N''-triisocyanato-

CLAIMS*nieuw claim!*

1. The process for the preparation of a coating, adhesive, film or sheet characterized, in that a mixture of a polyisocyanate functional, a polyepoxide functional, a polyanhydride functional or a polyketone functional compound or polymer and a compound containing reactive hydrogen, in which the compound containing reactive hydrogen is dispersed in a material which is non-reactive towards the compound containing reactive hydrogen, which mixture is not or low reactive at ambient conditions and high reactive under selected conditions, is applied onto a substrate at ambient temperature, followed by reacting the above compounds at elevated temperatures.

2. The process according to claim 1, characterized, in that at ambient temperature said compound containing reactive hydrogen is a solid material, a powder, a granule, a flake or grind or a mixture thereof which is preferably ground.

3. The process according to claims 1 and 2, characterized, in that the actual size of the grind of said compound containing reactive hydrogen, is from 0.5 to 200 μm and is preferably from 0.5 to 60 μm and is more preferably from 0.5 to 15 μm .

4. The process according to claims 1 to 3, characterized, in that said compound containing reactive hydrogen is a polyhydrazide, a polysemicarbazide, a polysulphonyl hydrazide, guanidine or a guanidine salt, a polyamine or blocked polyamine or is carbodihydrazide.

5. The process according to claim 4, characterized, in that said polyhydrazide is oxalic dihydrazide, malonic dihydrazide, succinic dihydrazide, adipic dihydrazide, sebacic dihydrazide, dodecanoic dihydrazide, isophthalic dihydrazide, piperazine N,N'-dihydrazide, m-benzene-dihydrazide, p-benzene-dihydrazide.

30

1 -- 4 ~~X~~ The process according to claims ~~X~~ or ~~X~~, characterized, in that the polyhydrazide is adipic dihydrazide or carbodihydrazide.

5-1-1 ~~X~~. The process according to claim ~~X~~, characterized, in that said polysemicarbazide is ethane-disemicarbazide, butane-disemicarbazide, propane-disemicarbazide, hexane-disemicarbazide, para-benzene-disemicarbazide, toluene-2,4-disemicarbazide, toluene-2,4-disemicarbazide, bis (4-semicarbazido-phenyl)ether, bis
10 (4,4'-hydrazido)-3,3'-dimethoxy biphenyl, di-N,N'-methylamino urea, 4,4'-methylene-bis(cyclohexene semicarbazide), 3-semicarbazido-methyl-3,5,5-trimethylcyclohexyl-semicarbazide or mixtures thereof.

7-1-1 ~~X~~. The process according to claim ~~X~~, characterized, in that said polysulphonyl hydrazide is p,p'-oxybis benzene sulphonyl hydrazide; bis(methylhydrazido)sulphate, bis (methylhydrazidosulphonyl)piperazine, bis p-(hydrazidosulphonylamino)benzene.

8-1-1 ~~X~~. The process according to claim ~~X~~, characterized, in that the guanidine salt is guanidine hydrochloride, guanidine acetate, guanidine carbonate, guanidine nitrate.

25 ~~X~~. The process according to claim ~~X~~, characterized, in that the the polyamine or polyamine salt is piperazine, piperazine diacetate, piperazine dihydrochloride, lysine, lysine hydrate, diaminoisophorone diacetate, diaminoisophorone dihydrochloride.

9 ~~X~~. The process according to claim 1, characterized, in that the material of claim 1 which ~~is non-reactive~~
10 ~~towards~~ said compound containing reactive hydrogen, is a polyether, a polyester, a polycarbonate, a polyacrylate, a polyvinylalkylether, a polyurethane, optionally substituted by substituents which are non reactive towards the material containing reactive hydrogen, and non- or low reactive
35 towards the isocyanate functional material or is a plasticizer of the group of phthalic alkylesters, adipic alkyl esters, sebacic alkyl esters, dodecanoic alkyl esters, polyesters, phosphate esters, fatty sters, straight

contains no groups which are reactive towards

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and modified natural or mineral oils, sulphonated oils, ethoxylated oils, epoxidised oils, fatty acids, sulphon amides, fat liquors, lecithine or a mixture thereof, optionally mixed with water.

10-5-9 ~~12~~. The process according to claims ~~1-11~~, characterized, in that the said mixture of the polyisocyanate functional, the polyepoxy functional, or the polyketone functional compound or polymer and the compound containing reactive hydrogen, is solvent free.

11-1-10 ~~13~~. The process according to claims ~~1-12~~, characterized, in that said polyisocyanate functional compound or polymer and said compound containing reactive hydrogen are mixed together in a ~~stoichiometric~~ ^{equivalent} ratio of 0.5 to 1.5, and preferably in a ratio of 0.9 to 1,1, applied onto 15 a substrate and the so obtained covered or impregnated substrate is heated to a temperature of 50 to 300 °C for 1 to ~~20~~ ¹⁰ min and preferably to a temperature of ~~20~~ ¹⁰ to 200 °C for 1 to ~~20~~ ¹⁰ min.

12-1-10 ~~14~~. The process according to claims 1-12, characterized, in that said polyisocyanate functional compound or polymer and said compound containing reactive hydrogen are mixed together in a equivalent ratio of 0.5 to 1.5, and preferably in a ratio of 0,9 to 1,1, and applied onto 20 a substrate whereafter the covered or impregnated substrate is immersed into water of 20 to 100 °C for 1 to 10 min.

13 ~~15~~. Coatings, coated substrates, adhesives, films, sheets, impregnated substrates, synthetic leathers, inmould coatings, coated leathers, coated polyvinylchlorides, coated non-wovens, coated coagulated polyurethane 30 substrates, breathable coated substrates, characterised, in that they are obtained by applying the process of any 12 of the preceeding claims 1-~~14~~.

~~16~~. A coating mixture comprising a mixture of a polyisocyanate functional compound, a polyepoxide functional 35 compound, a polyanhydride functional compound or a polyketone functional compound, and a compound containing reactive hydrogen which is not or low reactive at ambient temperature and highly r active under selected conditions,

hieuw claim 16 → word ^{is now} claim 14

which coating mixture is applied in the process of claim 1 to ~~25~~.

13

15 -- 1-14

~~25~~. A coating mixture according to claims ~~2-25~~, characterized, in that the mixture of the polyisocyanate functional compound, the polyepoxide functional compound, the polyanhydride functional compound or the polyketone functional compound or polymers thereof and the compound containing reactive hydrogen is stable at ambient temperature for at least one day.

16 - 10
-- 14
-- 15

~~25~~. A coating mixture according to claims ~~25~~ or ~~26~~, characterized, in that the mixture of the polyepoxide functional compound, the polyanhydride functional compound or the polyketone functional compound or polymers thereof and the compound containing reactive hydrogen is stable at ambient temperature as a one pot system.

15

17 14-16

~~25~~. A coating mixture according to claims ~~25-26~~, characterized, in that the compound containing reactive hydrogen is present as grind which is dispersed in a material which is non-reactive towards the material containing reactive hydrogen.

20

18 14-16

~~25~~. A coating mixture according to claims 16-18, characterized, in that at ambient temperature the compound containing reactive hydrogen is a solid, which is a powder, a granule, a flake or a grind or a mixture thereof, which is preferably ground.

25

19. 14-16

~~25~~. A coating mixture according to claims ~~15-18~~, characterized, in that the particle size of the ground or of the dispersion of the compound containing reactive hydrogen is from 0,5 to 200 μm , preferably from 0.5 to 60 μm and most preferably from 0.5 to 15 μm .

30

08. 10. 2001

N w claims

(45)

Druckexemplar

Claim 1:

1. The process for the preparation of a coating,
5 adhesive, film or sheet characterized, in that a mixture
of a polyisocyanate functional, a polyepoxide functional,
a polyanhydride functional or a polyketone functional
compound or polymer and a dispersion of a compound
containing reactive hydrogen, which compound is a
10 polyhydrazide, a polysemicarbazide, a
polysulphonylhydrazide, carbodihydrazide, in a material
which contains no groups which are reactive towards the
compound containing reactive hydrogen, in which mixture
the reactivities of the isocyanate, epoxide, anhydride or
15 the ketone functions towards the hydrazide, semicarbazide,
sulphonylhydrazide or carbodihydrazide is absent or low at
ambient conditions and the reactivities are high at
temperatures of 50 to 300 °C, is applied onto a substrate
at ambient temperature, followed by reacting the above
20 compounds at 50 to 300 °C for 1 to 10 min, or is applied
onto a substrate at ambient temperature, followed by
immersing the coated substrate into water of 20 to 100 °C
for 1 to 10 min.

25 Claim 11:

The process according to Claim 1, characterized
in that the material which contains no groups which are
reactive towards the compound containing reactive
hydrogen, is a
30 polyether, a polyester, a polycarbonate, a polyacrylate, a
polyvinylalkylether, a polyurethane, a polyacrylate, a
polyvinylalkylether, a polyurethane, optionally
substituted by substituents which are non reactive towards
the material containing reactive hydrogen, and non- or low

reactive towards the isocyanate functional material or is a plasticizer of the group of phthalic alkylesters, adipic alkyl esters, sebacic alkyl esters, dodecanoic alkyl esters, polyesters, phosphate esters, fatty esters, 5 straight and modified natural or mineral oils, sulphonated oils, ethoxylated oils, epoxidised oils, fatty acids, sulphon amides, fat liquors, lecithine or a mixture thereof, optionally mixed with water.

10 Claim 16:

A coating mixture to be applied in the process of claim 1 to 15 wherein the coating mixture comprises a mixture of a polyisocyanate functional, a polyepoxyde functional, a polyanhydride functional or a polyketone 15 functional compound and a dispersion of a compound containing reactive hydrogen , which compound is a polyhydrazide, a polysemicarbazide, a polysulphonylhydrazide, carbodihydrazide, in a material which contains no groups which are reactive towards the 20 compound containing reactive hydrogen, in which mixture the reactivities of the isocyanate, epoxide, anhydride or the ketone functions towards the hydrazide, semicarbazide sulphonylhydrazide or carbodihydrazide is absent or low at ambient conditions and the reactivities are high at 25 temperatures of 50 to 300 °C or when the mixture is immersed into water.